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Technological Alternatives for the Conservation of Strategic and Critical Minerals—Cobalt, Chromium, Manganese, and Platinum-Group Metals: A Review

By Russell J. Foster

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES 75TH ANNIVERSARY

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By Russell J. Foster

UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary

BUREAU OF MINES
Robert C. Horton, Director

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As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering the wisest use of our land and water resources, protecting our fish and wildlife, preserving the environmental and cultural values of our national parks and historical places, and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to assure that their development is in the best interests of all our people. The Department also has a major responsibility for American Indian reservation communities and for people who live in Island Territories under U.S. administration.

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mt	metric ton
°F	degree Fahrenheit	pct	percent
ft	foot	st	short ton
kW	kilowatt	tr oz	troy ounce
lb	pound	wt pct	weight percent
m	meter	yr	year

TECHNOLOGICAL ALTERNATIVES FOR THE CONSERVATION OF STRATEGIC AND CRITICAL MINERALS--COBALT, CHROMIUM, MANGANESE, AND PLATINUM-GROUP METALS: A REVIEW

By Russell J. Foster[1]

ABSTRACT

This Bureau of Mines review focuses on the extent to which technologically and economically feasible programs in substitution, improved processing practices, including recycling, and design can achieve conservation of cobalt, chromium, manganese, and platinum-group metals, and thus reduce U.S. vulnerability to interruptions of supply. In addition, supply-side options--domestic and foreign resources, ocean minerals, and stockpiles--are identified. The report consolidates four major studies on these strategic and critical minerals sponsored entirely or partially by the Bureau in the last few years. These studies have been updated with further information from the recent literature.

[1]Physical scientist, Branch of Technical Analysis, Bureau of Mines, Washington, DC.

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INTRODUCTION

Recently there has been an increase in public awareness of the importance of nonfuel minerals to the well-being of the United States. The specific issue of strategic and critical minerals availability has generated much interest and controversy, as evidenced by the increasing volume of literature and the numerous conferences, workshops, and symposia convened on the subject. The Bureau of Mines, as part of its continuing role to identify and analyze problems and policies regarding the Nation's mineral requirements, has been an active participant in this area.

Always included in any list of strategic and critical minerals are cobalt, chromium, manganese, and platinum-group metals. The United States relies on imports for nearly all of its requirements for these materials, and most of the principal sources of supply are remote and located in regions that have a relatively high risk of political instability. Supply disruptions could adversely affect the manufacture of important products for the economy and national defense.

Cobalt is used in alloys for strength and heat and wear resistance, as a binder in cemented carbides, for magnetic and catalytic materials, and in paint driers. Chromium is used as an alloying element in stainless and alloy steels, as chromite refractories to line high-temperature furnaces, and to make chemicals for pigments, plating, and leather tanning. Manganese is important for its desulfurizing, deoxidizing, and alloying functions in iron and steelmaking; other uses of manganese are dry cell batteries and chemicals. The platinum-group metals exhibit several remarkable properties including resistance to high-temperature corrosion and oxidation, extensive catalytic activity, and high melting points, which enable them to be used as automotive, chemical process, and petroleum refining catalysts; in electrical and electronic devices, dental materials, and jewelry; and for glass manufacturing.

The utilization of technological alternatives--substitution and conservation--presents a means of lessening the vulnerability of the United States to interruptions of supply.

Current essential U.S. cobalt needs are estimated at about 50 pct of present consumption. Existing technology is capable of achieving cobalt savings of over 10 million lb annually by the next decade.

Present U.S. chromium consumption could be reduced by approximately one-third by using available technology to substitute alternative materials and processes, to recover and recycle waste chromium, and to design for greater chromium efficiency.

From a practical standpoint there is no substitute for manganese in steelmaking. However, the recent adoption of new steelmaking practices has been a major factor in substantially reducing the unit consumption of manganese per ton of raw steel produced.

Platinum-group metals exhibit excellent recyclability. Automotive catalytic converters represent a considerable source of platinum-group metals, but the low concentration of the metals and the logistics of converter collection are obstacles to recycling.

Domestic deposits of these minerals would require market prices substantially in excess of those currently prevailing to warrant development. Bringing individual sites on-stream would generally require several years.

BACKGROUND

THE IMPORTANCE OF MINERALS

The United States requires a continuous and substantial supply of minerals to sustain the domestic economy and maintain the national defense. In 1983 the crude nonfuel mineral production[2] of the United States was valued at $21.1 billion ($19.7

[2]Production as measured by mine shipments, sales, or marketable production (including consumption by producers).

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billion in 1982, despite an economic recession). These minerals were used as inputs for products which contributed over $200 billion to the U.S. gross national product. Viewed in the context that a strong economy is essential to facilitate the development of defense materiel and to provide a defense mobilization base, it has been stated that "...adequate supplies of virtually every known material are a strategic necessity" (1).[3]

In a narrower perspective, strategic and critical minerals are considered to be those for which National Defense Stockpile goals have been established. The Strategic and Critical Materials Stock Piling Revision Act of 1979 defines strategic and critical materials as those that (1) would be needed to supply the military, industrial, and essential civilian needs of the United States during a national defense emergency and (2) are not found or produced in the United States in sufficient quantities to meet such needs.

Even among the materials in the stockpile there is a hierarchy with regard to their level of "criticality" (2-6). Some of the criteria usually considered include the importance of the material to the economy (even a disruption cost that is small relative to the economy as a whole can still be substantial for a given industry or region); importance to the national defense (minerals that are essential to certain defense uses may not play a similar role in the context of overall economic activity); the attendant social and political (noneconomic) effects of a disruption; demand trends; domestic reserves and resources (cost of exploration, probability of discovery, availability); domestic capacity (mine, processing, fabricating); magnitude of import reliance; foreign supplier countries (number, capacity, accessibility, ideology, political and economic stability); substitutability (present availability, cost and time to develop); recyclability; stockpiles (Government, industry). While basic materials such as iron, copper, and lead certainly are of importance to the Nation, others such as cobalt, chromium, manganese, and platinum-group metals assume more prominent positions from the perspective of possible supply problems.

IMPORT DEPENDENCY AND VULNERABILITY (5, 7-10)

Since there is no uniformity in the qualitative and quantitative geologic distribution of the earth's mineral resources, no country is self-sufficient with regard to mineral requirements. The degree of import reliance varies considerably among the highly industrialized nations. The resource policy of the U.S.S.R., for example, has been characterized by a willingness to incur substantial costs in order to promote a balanced development of all the materials required by an industrialized society; only when extremely high costs have been encountered has the Soviet Union been willing to accept some degree of reliance on foreign supplies (11). Japan, on the other hand, is basically a mineral-resource-poor country, heavily dependent upon raw material imports, and involved in many foreign mineral ventures. The United States has substantial mineral resources and has developed a large, multifaceted minerals industry, but still relies in varying degrees on imports to supply a number of minerals, including several used in key sectors of the economy and defense. Although some U.S. mineral imports are necessitated by inherent resource limitations, others are based on economic advantage. As the Nation's import dependence becomes greater, however, in terms both of the number of minerals involved and the percentage of demand that is satisfied by imports, the possibilities for supply difficulties increase. Minerals availability problems can result from periods of unusually strong demand, labor strikes, natural disasters, cartel actions, military conflicts, politically motivated pressures, and internal strife. An additional factor is the concept of a "resources war," which proposes that the Soviet Union,

[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

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through its influence with certain mineral-producing nations or their adversaries, may be in a position to selectively exert control over the flow of certain strategic and critical materials to the United States and its allies. Import dependency in itself is not necessarily a problem, but the position changes to one of vulnerability when the need for a material is such that a supply interruption would have severe economic and/or defense implications; the possibility of an interruption is enhanced by the actual or potential instability or unreliability of the supplier; domestic resources and foreign alternative supply sources are inadequate; and substitutability is limited. The oil embargo initiated by Arab states in 1973 graphically demonstrated the significant impact that a supply shortage of a vital material can have. Likewise, the recent supply and price instabilities in the cobalt market showed that the availability of certain nonfuel minerals cannot be taken for granted.

SUPPLY-DEMAND ALTERNATIVES (5, 12-24)

Despite the fact that achievement of self-sufficiency in minerals and materials is unlikely for the United States, steps can be taken to lessen import vulnerability. These steps basically consist of reducing consumption through technological options and innovations in the areas of substitution[4] and conservation (improved processing practices, recycling, and product design), and assuring the accessibility of primary supplies by developing alternative domestic and foreign mineral deposits and through stockpiling.

[4]Many analysts discuss substitution and conservation as separate entities, but strategic substitution can be considered as a form of conservation. Although substitution may not reduce the overall use of materials, it can effectively reduce the requirements for a particular material by shifting the burden to one less critical.

Substitution

Substitution has both engineering and economic aspects--technical performance and cost effectiveness must be considered. The time needed to develop a substitute and to implement a successful substitution program can be considerable, particularly if new technology also is required. Under normal conditions, substitution is a dynamic displacement process that occurs over time as a consequence of changing conditions such as the relative price of materials, technological advances, consumer preference, and Government regulation.

Substitution is not a viable short-term solution to a sudden material shortage or price escalation unless the substitute possesses well-established properties and performance comparable to the preferred material; requires only minimal changes in existing technology and processing and fabricating facilities; and is readily available at reasonable cost from domestic or accessible, reliable, foreign sources. Substitutes for strategic and critical materials rarely meet these criteria--the alternative material usually is less attractive both technologically and economically. Essential uses for a material are those that are not substitutable--such a material has a unique chemical or physical property, or functions on a scale or at a price that cannot be met by any other.

Processing

Losses of material occur at all stages of the materials cycle, from extraction of ore and conversion into intermediate forms, through fabrication of the finished product, to eventual disposal or recycling. Significant losses occur in mining, milling, concentrating, and smelting, as fairly large amounts of material are discarded in mine and mill tailings and slag, but the cost of further incremental recovery is relatively high. Therefore, conservation efforts are most often directed at the materials

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fabrication stage. Of course, in the case of those strategic and critical minerals where domestic production is nonexistent, processing options are effectively limited to fabrication.

Conservation is especially prominent in the metallurgical area, where the benefits of new processing technologies include improving product yield with continuous casting; minimizing alloying element loss through sophisticated melting (vacuum induction melting, vacuum arc remelting, electroslag remelting) and refining (argon-oxygen decarburization, vacuum-oxygen decarburization) steps, and surface modification techniques (cladding, lining, coating, surface impregnation); reducing scrap in fabrication with near-net-shape technology (investment casting, powder metallurgy); and improving quality control.

Recycling

Recycling offers an opportunity to provide extended or alternative uses for a material. Effective recycling conserves not only the material itself, but in some cases energy as well, and can have the added benefit of improving environmental quality. However, the extent of recycling (i.e., home, prompt industrial, or obsolete scrap) depends upon relative primary metal prices, collection logistics, and available technology. Barriers in the form of laws, regulations, and policies also can place secondary materials at a competitive disadvantage to their primary counterparts (17).

Design

Design is a basic determinant of materials use. Products and systems can be designed with an underlying conservation philosophy based on materials criticality, reliability, and recyclability, but under conventional circumstances where preferred materials are accessible the designer is concerned primarily with cost and performance considerations.

Domestic Supply

The development of domestic primary supply capability for strategic and critical minerals offers a far more secure and accessible alternative to unreliable or potentially unstable foreign sources, but establishing domestic mineral production capacity may not be economically feasible and also can require a great deal of time. Regulations and restricted access to public lands can further deter domestic mineral production. Even if developed, domestic deposits may be capable of satisfying only a modest share of consumption and/or may face rapid depletion. Nevertheless, established institutional means, in the form of the Defense Production Act, exist to provide subsidization of domestic mineral production. Title III of the act specifically authorizes the President to institute and maintain programs of financial assistance for the expansion of domestic production capacity and supply.

Foreign Supply

The reliability of foreign sources of supply is the crux of import dependency versus vulnerability. Obviously, risk can be minimized by diversifying supply sources among stable, friendly nations where possible. However, ensuring the development of an alternative foreign source of mineral supply and the continued viability of the operation in a competitive world market may require direct financial or technical assistance, or a long-term, guaranteed purchase agreement on the part of the United States.

In some instances, primary raw materials imports are being displaced by imports in the form of processed products, such as ferroalloys. There is a clear and accelerating trend for ore-producing countries to convert ore to higher valued intermediate products. This aspect of foreign supply has complex industrial and national security policy implications: Concentration of processed materials

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capacity outside the United States is leading to further import dependence and possibly vulnerability, and, by displacing domestic capacity, is contributing to the erosion of the Nation's industrial base. Furthermore, minerals in the National Defense Stockpile are of little utility without adequate processing capability. Government options available include domestic conversion of stockpiled ore to intermediate products; import tariffs or quotas; and maintenance of a minimum level of capacity by directed purchasing or facility acquisition.

Ocean Minerals

Much of the interest in unconventional mineral resources--those that differ significantly from productive deposits in either mineralogy or geologic setting--centers on ocean minerals. Manganese nodules and crusts represent some of the world's largest untapped deposits of important metals. Pacific Ocean nodules typically contain about 0.1 to 0.5 pct Co, 25 to 35 pct Mn, 1 to 1.5 pct Ni, and 1 to 1.5 pct Cu on a dry basis (24); the nodules and crusts off the southeastern shoreline of the United States and south of Hawaii contain less manganese, but some are cobalt-rich. However, the potential of ocean mining is clouded with uncertainty. Although technically feasible extractive processes exist, the technology and logistics of mining and transport are complex and expensive. Under present market conditions, the economics of developing the mineral resources on the ocean floor are unfavorable, and the unsettled international legal status of deposits outside the Exclusive Economic Zone (EEZ) presents a further complication.

Stockpiles

The availability of materials also can be increased by accumulating stockpiles to be held for release in times of short supply. The National Defense Stockpile, however, exists to supply military, essential civilian, and basic industrial needs of the United States during a national defense emergency, and by law cannot be used for economic or budgetary purposes (24). This greatly limits the accessibility of stockpile materials. Since 1939, there have been 28 releases from the stockpile, but only 4 have occurred during peacetime. Some stockpile materials lack immediate usefulness in terms of form if ore is held rather than processed materials without adequate domestic processing capability, and in terms of specifications if material acquired years ago has since been rendered obsolete by technological developments.

Private industry stockpiling has been proposed as a reliable supplement to the National Defense Stockpile. Consuming companies are intimately acquainted with the materials used in their own manufacturing processes, so they should be able to privately stockpile materials of optimum quantity, quality, and form for their use at any given time. However, when minerals availability is high and prices are low, concerns about stockpiling are minimal. Also, the cost of maintaining large inventories could be prohibitive for the private sector.

PERSPECTIVES

The issue of strategic and critical minerals availability has evoked a spectrum of opinion regarding the likelihood and consequences of supply disruptions. The economy of the United States probably could adapt to most supply disruptions, but depending on the material involved, the time required for such adaptation could be lengthy, severe economic dislocations might occur, and the noneconomic ramifications could be of equal or greater importance.

The United States has historically been a net importer of several important minerals, but it is improbable that major inroads into import dependence will be made by the private sector during times when minerals are readily available at low cost. The principal impediment to conservation is that there are few inherent incentives other than the economic factors of the market itself. Even minimal levels of resource exploration and substitution preparedness are expensive ventures with no assurance of eventual

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success or utility. However, "on-the-shelf" technology and existing stockpiles (provided that the form and specifications of the stockpiled material are optimally matched to needs) are the only short-term supply-demand solutions to a disruption. Other technological measures are ineffective if they are not undertaken until the onset of the problem.

Therefore, it appears necessary to have continued foresight and awareness of possible materials shortages, and plan contingency strategies so that otherwise manageable situations do not become crises because of inadequate lead time. The characteristics and applications of the individual materials themselves will determine the optimum approach, but if these strategies involve conservation and substitution research and mineral exploration, the Government will have to make a commitment to an active role.

Invariably included among the materials considered important to the Nation's industry and defense, and most vulnerable to potential supply disruptions, are cobalt, chromium, manganese, and platinum-group metals. They are discussed individually in succeeding chapters.

COBALT

BACKGROUND

Cobalt imparts strength and heat and wear resistance to certain alloys. It is also a strongly magnetic element and displays catalytic activity. As a result, cobalt has a number of important uses including superalloys (gas turbine engines), wear-resistant alloys, tool steels, cemented carbides (tools, mining and drilling equipment), magnets, (rotating machinery, indicating meters, telecommunications, loudspeakers), catalysts (petroleum, chemicals), and paint driers. The magnitude of domestic cobalt consumption by end use is shown in table 1. The cobalt resources of the United States cannot be considered reserves at current prices and with existing technology, and there has been no domestic mine

TABLE 1. - U.S. consumption[1] of cobalt, by end use

(Thousand pounds of contained cobalt)

End use	1981		1982		1983	
	Quantity	pct	Quantity	pct	Quantity	pct
Superalloys	4,195	36	3,319	35	4,034	36
Magnetic alloys	1,687	14	1,544	16	1,711	15
Cemented carbides	1,076	9	638	7	666	6
Wear-resistant alloys (hardfacing)	488	4	446	5	472	4
Tool steels	170	1	161	2	248	2
Other steels	176	2	165	2	54	.5
Nonferrous and other alloys	254	2	201	2	241	2
Catalysts	1,279	11	789	8	1,064	9
Paint driers	1,378	12	1,114	12	1,503	13
Pigments	329	3	382	4	366	3
Ground-coat frit	441	4	477	5	651	6
Glass decolorizers	40	.3	32	.3	41	.4
Animal feeds	58	.5	52	.6	51	.4
Miscellaneous	109	1	148	2	217	2
Total[2]	[3]11,680	100	[3]9,468	100	[3]11,319	100

[1]Reported consumption.

[2]Data may not add to totals shown because of independent rounding.

[3]Calculated apparent consumption, based on production, import and export data, stockpile acquisitions, and stock changes, was 12.5 million lb in 1981, 11.5 million lb in 1982, and 15.7 million lb in 1983.

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production of cobalt since 1971. As a result the United States relies on imports for nearly all of its cobalt requirements--net import reliance has averaged over 90 pct for the past several years--and two of the principal sources of supply, Zaire and Zambia, are remote, developing countries in a region where political instability is a potential risk.

Calculated apparent consumption of cobalt in the United States was 15.7 million lb in 1983, far below the alltime high of 23.7 million lb in 1974. Nevertheless, it represented a marked increase over the 1982 total of 11.5 million lb which was the lowest quantity consumed since 1961. The producer price stabilized at $12.50/lb during 1983, but the spot-market price was much lower, ranging from $4.75/lb to $6.40/lb.

The cessation of stockpile sales of cobalt prior to 1977, and a subsequent period of rapidly increasing demand, eventually led Zaire to initiate an allocation program in May 1978. Shortly thereafter, a brief military invasion of Zaire's Shaba Province resulted in a temporary shutdown of cobalt operations. Although these events actually had minimal impact on cobalt production, consumers' concerns for the availability of cobalt sent producer and spot-market prices up dramatically, to $25/lb and over $40/lb respectively. Subsequent conservation efforts coincided with an economic downturn to significantly reduce cobalt demand, and, beginning in 1981, prices responded accordingly. Despite the recent trend of declining consumption, U.S. demand for cobalt is forecast to increase at an annual rate of 2.7 pct from 1981 to the year 2000. The world production of primary cobalt, world cobalt reserves, and exports to the United States are listed in table 2.

USES AND DEMAND ALTERNATIVES

Superalloys (24-26)

Cobalt is used in many superalloys to enhance their high-temperature properties and processability. With respect to cobalt, superalloys can be classified as cobalt-base (40 pct or more Co) and cobalt-bearing, nickel-base (8 to 20 pct Co). The major use of superalloys is in gas turbines, principally for jet aircraft engines, and to a lesser extent for other propulsion systems, power generation, and gas compression. Much of the alloy substitution that could readily take place occurred during the 1978-80 period. Limited laboratory results from NASA's Conservation of Strategic Aerospace Materials (COSAM) program, which has the objective of minimizing the strategic metal content of vital aerospace components (27), have shown that current U.S. superalloys may contain about 50 pct more cobalt than is necessary for most applications, but the potential for using further substitutes for cobalt in superalloys is limited in the short term, especially for aircraft applications, because of the stringent standards, high costs, and long lead times required to certify substitute alloys. The current engineering of superalloys is dictated more by the need to meet stringent property and reliability specifications than by economic or conservation considerations. With only 200 to 900 lb of cobalt required for a multimillion-dollar jet engine, materials costs will not drive the designer toward an alternate selection unless a parallel alloy and process that can be readily put to use have been established. Otherwise, only a major systems benefit can provide sufficient incentive for change. A ceramic gas turbine engine can operate at higher temperatures and therefore greater thermal efficiency than its metallic counterpart (28). Ceramics also provide improved corrosion resistance and lower density. However, because of their brittleness, ceramics as yet do not offer the durability and reliability required for long-term applications, such as aircraft engines.

Many superalloys are used with protective coatings, some of which are themselves cobalt-rich. The possibility of using other metallic coatings in place of cobalt depends on the particular application for which the coating is intended. For high-temperature oxidation (oxygen environment) cobalt could be replaced by

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TABLE 2. - World cobalt mine production, reserves, and U.S. imports

(Thousand pounds of contained cobalt)

Country	Mine output			Reserves	U.S. imports		
	1981	1982[P]	1983[e]		1981	1982	1983
Australia	3,672	3,990	4,000	50,000	83	169	168
Belgium-Luxembourg	0	0	0	0	939	613	1,123
Botswana	560	560	560	20,000	633	364	400
Brazil	NA	NA	260	NA	0	0	0
Canada	4,586	3,096	3,492	100,000	1,846	1,483	1,950
Cuba	3,780	3,300	3,640	400,000	0	0	0
Finland	2,280	2,050	2,000	50,000	1,206	798	1,017
France	0	0	0	0	367	336	91
Germany, Federal Republic of	0	0	0	0	213	255	79
Greece	0	0	0	30,000	0	0	0
India	0	0	0	40,000	0	0	0
Indonesia	0	0	0	400,000	0	0	0
Japan	0	0	0	0	1,624	1,024	462
Morocco	1,740	1,540	0	0	0	0	0
Netherlands	0	0	0	0	64	28	507
New Caledonia	814	598	600	500,000	87	0	0
Norway	0	0	0	0	1,631	852	707
Philippines	2,198	1,258	1,320	300,000	0	0	0
South Africa, Republic of	0	0	0	40,000	464	266	185
U.S.S.R.	4,800	5,000	5,200	300,000	0	0	0
United Kingdom	0	0	0	0	599	271	367
Yugoslavia	0	0	0	20,000	0	0	0
Zaire	34,000	24,920	24,920	3,000,000	4,176	4,971	7,723
Zambia	7,530	7,160	7,060	800,000	1,513	1,164	2,347
Zimbabwe	220	220	140	5,000	0	0	32
Other	0	0	0	NA	149	276	64
Total	66,180	53,692	53,192	[1]6,000,000	15,594	12,870	17,221

[e]Estimated. [P]Preliminary. NA Not available. [1]Rounded.

iron or nickel with little or no loss in usable life. In a high-temperature, sulfidic corrosion environment, replacement of cobalt would definitely decrease coating service life. Although cobalt-base coatings are used in low-temperature corrosive environments, cobalt may not be necessary. Ceramic thermal barrier coatings may permit cobalt to be replaced in some environments provided repeated thermal cycles can be tolerated. The effect on coatability of decreased cobalt in the substrate alloy also must be considered, but the presence or absence of cobalt in alloy substrates or coatings does not appear to have much bearing on the processability of coatings using advanced coating techniques.

The superalloy industry generates a high proportion of scrap and waste because of the large number of different and complex alloys produced and the use of composites. Efforts directed at reducing the amount of scrap have taken the form of a continuing trend to production of "near-net-shape" components--substitution of investment castings for forgings and the recent development of powder processing. In addition, modern melting and analytical methods have significantly reduced off-spec heats; vacuum or controlled atmosphere teeming greatly reduces ingot defects; care is taken to minimize the quantity of material removed with end crops, edge trimming, and finish conditioning. These are evolutionary changes already well under way that may reduce the actual quantity of in-house scrap produced by 25 pct. The best opportunity for significant further

reduction in scrap is the adoption of near-net-shape processing for a wider variety of shapes and components. Scrap recycling is an established practice in the superalloy industry. The materials recycled are solid metallic scrap from primary production sources--the predominantly clean, well identified solids and processed turnings which are relatively easy to collect, handle, verify (composition), and melt. However, approximately 40 pct of wrought superalloy scrap and 50 pct of cast superalloy scrap is not directly recycled domestically for production of these alloys. It is downgraded for use in the steel industry, lost, or exported. Dusts, grindings, furnace scale, and pickle sludges are often mixtures of every alloy produced in the plant and hence are low grade, finely divided, and costly to dry, with inherently limited use for recycling. Obsolete scrap solids are not efficiently recycled--turbine components may become contaminated in service with elements such as lead and sulfur that are highly detrimental to superalloy properties; separation of superalloy components that have been fabricated into more complex assemblies by welding, brazing, or coating can be difficult; the collection of obsolete scrap on a small scale presents logistical difficulties. The best prospect for improving cobalt recovery for use in superalloys is improving the efficiency of recovering obsolete solid scrap, and it is likely that a greater proportion of obsolete scrap solids will be directly recycled in the future. However, a significant amount will continue to be downgraded--a number of processes for separating individual elements from complex superalloy scrap have the ability to recover some or all elements in a purity suitable for use in superalloys, but commercial-scale plants are marginally economic.

Magnetic Alloys (24-26)

Cobalt is the strongest magnetic element. It increases the saturation magnetization of iron and has the highest Curie temperature known. Therefore, permanent magnets made with cobalt are generally superior. The principal magnet applications are rotating machinery, indicating meters, telecommunications, and loudspeakers. The largest use of cobalt in magnetic devices is in Alnico permanent magnets (alloys of iron, nickel, cobalt, aluminum, and lesser amounts of other elements). Together with iron-chromium-cobalt deformable magnets they total about 90 pct of cobalt used in magnetic applications. Iron-chromium-cobalt alloys offer magnetic characteristics nearly identical to Alnico but at much lower cobalt content. These types have a magnetic energy density 3 to 4 times greater than that of Alnico with only double the cobalt content and are well suited for small, high-torque, fast-response, electric motors. Soft cobalt-containing magnetic materials (e.g., 2V Permendur, Supermendur) find minor use in aircraft generators and telephone receiver diaphragms; semihard cobalt-containing magnetic materials (e.g., Remendur, Nibcolloy) find minor use in reed switches, memory applications, and hysteresis motors.

A number of parameters must be considered when magnetic materials are specified for any given application--magnetic strength, size, operating conditions, and cost. Yet, the magnetics industry has reduced its dependence on cobalt through the use of low- or no-cobalt substitutes more than any other industry.

Hard ferrites (ceramic magnets) have virtually replaced Alnicos in all large loudspeakers. For smaller speakers iron-chromium-cobalt magnets are feasible, and for the smallest speakers rare earth-cobalt magnets have merit, but further substitution is unlikely at current cobalt prices. Modest substitution could occur at 3 times current prices, but even at 10 to 20 times current prices about 10 to 20 pct of the loudspeakers would still require cobalt.

Rotating machinery utilizes primarily permanent magnet generators, motors, and magnetos. Hard ferrites are widely used up to 10 kW power because of cost effectiveness. Greater than 10 kW power demands high-energy-density magnets,

particularly rare earth-cobalt. At a tenfold cobalt price increase strenuous efforts would be made to use cobalt-free, or cobalt-efficient, materials, or possibly revert to electromagnetic designs, although about 10 to 20 pct of the market could justify cobalt.

The designs of certain instruments and indicating meters are closely tied to specific materials. Only at 10 times the present cobalt price would the use of more cobalt-efficient materials occur, and the development of new meter designs operating on different principles be considered.

In the field of telecommunications the potential for less cobalt use is substantial. Technological changes such as miniaturization, large-scale integration, digital signaling, and photonics will greatly reduce cobalt requirements.

The magnetic industry makes effective use of home or runaround scrap generated during magnet manufacture, but there is little recycling of obsolete scrap except large magnets in scrapped equipment and magnets in leased equipment such as telephones. Public utilities could do the same with damping magnets in watt-hour meters, but cobalt prices would have to increase at least threefold. The primary barriers to recycling are identification and collection of obsolete scrap from widely dispersed locations and the cost of removing small components from scrapped units.

Cemented Carbides (24-25)

Cobalt is used as the binder in the structure of cemented tungsten carbides in amounts ranging from 3 to 25 pct. These alloys are characterized by exceptional combinations of hardness, temperature and abrasion resistance, high elastic modulus, strength, and toughness, and are widely used in tools for machining cast iron and nonferrous metals, metal forming, mining, oil and gas well drilling, and a variety of highly stressed structural applications. In machining ferrous metals, additions of titanium carbide, tantalum carbide, and columbium carbide are employed to improve the cutting tool's resistance to chip erosion ("cratering") and to the effect of high cutting-edge temperatures generated during the machining operation.

Substitution of other binder metals and alloys in cemented carbides has received the concentrated attention of researchers over the past 60 yr. In certain cemented carbide alloys designed to combat combined corrosion and abrasion, nickel and iron have shown the most promise as substitutes with chromium additions to impart corrosion resistance. Titanium carbide-base cemented carbides commonly containing nickel as the binding metal have found an important but small and specialized field of use. The same is true of aluminum oxide-base ceramics and titanium carbide-aluminum oxide "cermets." Other materials receiving attention for specialized uses include silicon nitride as a base compound for cutting tool materials and polycrystalline diamond and cubic boron nitride cutting tools for specialized areas of metal and composite material cutting. However, these are not capable of mass replacement of cobalt-bearing cemented carbides without an unacceptable loss of productivity and economy in metal cutting because of their brittleness and low cutting-edge strength. Coal and hard-rock mining and oil and gas well drilling applications depend on the unique combination of properties possessed by tungsten carbide-cobalt alloys. Cobalt remains the superior binder, and there are no apparent practical alternatives available or in sight today. The same is true for certain metal-forming and superpressure applications. Research on replacements for cobalt as a binding metal is primarily motivated by the desire to improve properties (corrosion resistance) of currently available alloys, and to reduce risks associated with dust exposure.

Virtually all cemented carbide manufacturing scrap is recycled. However, obsolete scrap recycling is less extensive because of the wide dispersion of carbide users. Nevertheless, direct recycling of obsolete cemented carbide scrap has become established with several process routes available. The current practical

limit of cemented carbide scrap that is recycled ranges from 15 to 80 pct depending on the application. Although theoretical maxima can reach 65 to 95 pct, the probable practical limit is estimated at 40 to 85 pct.

Wear-Resistant Alloys (24-26)

The composition of the most commonly used wear-resistant (hardfacing) alloys is 50 to 70 wt pct Co for application in automotive engine valves, fluid valves, knives, cutters, erosion shields, hot-working dies, and bearing surfaces that cannot be lubricated. The mode of wear--abrasive, adhesive, or erosion--determines the criticality of cobalt use. Cobalt offers important performance benefits against galling and cavitation erosion wear, but alloys with lower cobalt levels provide alternatives. For erosion from particle impingement there also exist opportunities for alternative alloys with lower or no cobalt. Nickel-base alloys are gaining in hardfacing of automotive engine valves and valve-seat inserts. The nickel-base properties are comparable or better, are lower cost, and are more easily processed as powder. However, at current cobalt prices there is little incentive to replace high-cobalt wear-resistant alloys with alternatives. In addition, the performance of cobalt alloys is well established. Should cobalt prices increase, so would the incentive for substitution. At 10 to 15 times current prices, efforts to use substitutes would sweep all areas of wear application, and up to half the cobalt currently used could be conserved.

Hardfacing and coating alloys are often utilized as powder metallurgy products deposited as plasma or flame-sprayed powders. The system typically does not recycle the overspray, the scrap, or hardfacing or coating material from obsolete parts. Hardfacing rod made by continuous casting and typically used in valve seats and components for diesel engines is not recycled once the seats are taken out of service because of high iron contamination, since the alloy is hardfaced onto an iron substrate.

Steels

Tool Steels (24-26, 28)

Tool steels are metallurgically complex with six or more major alloying elements and a large number of commercially recognized compositions. Raw materials represent a fraction of overall production costs because of the special processing involved, so improved performance can often justify the use of high-cost materials. The heat generated in the machining of some materials (stainless steels, superalloys, titanium alloys), can soften the tool steel so that performance deteriorates. Cobalt is added (5 to 12 pct) to high-speed tool steels to increase attainable hardness and improve hot hardness and hardness retention, thus improving tool life. Except for high-speed tool steels the only cobalt-bearing standard grades of tool steels are hot-work and cold-work tool steels, and the amount of cobalt in them is minor compared to the high-speed tool steels. Comparable cobalt-free high-speed steels have been developed, so the presence of cobalt is not essential, and its use can be determined by economic considerations. The development of coatings (titanium carbide, titanium nitride) that increase tool life also will minimize the need for cobalt-bearing steels.

Opportunities for reduction of scrap generated during conventional processing are limited. New processing methods, such as electroslag remelting, have provided better product yield and hence less scrap. Further improvement in yield can be expected from the adoption of semicontinuous casting of intermediate-size billets, or powder metallurgy, but neither process comes close to entirely eliminating scrap. Although a substantial portion of tool steel scrap is recycled, the efficiency of recovery of the alloying elements is significantly lower than with superalloys. Almost all solid in-house scrap and prompt industrial scrap solids are separated by grade and recycled (remelted). Some obsolete scrap, primarily large monolithic industrial cutting tools, is also recycled. Particulate

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scrap such as furnace dust and mill scale is generally collected with other tool steel and alloy steel wastes produced by the mill, but oily grindings produced by tool fabricators are not recycled because of their high residual phosphorus content, which is unacceptable to tool steel manufacturers. Theoretically all tool steel scrap could be carefully identified during collection and recycled directly or after further processing. However, the fact that it is so often mixed with much lower grade scrap makes more efficient collection impractical. Improved sorting and identification techniques have made it possible to recover virtually all solid scrap for recycling directly within the mill. Research aimed at devising methods of treating tool steel grindings to make them suitable for recycling is underway. Procedures for recovering mixed alloy sludges generated by electrical discharge machining processes are also likely to be developed in the next few years. Some work has been done on the chemical separation of the elements in tool steel scrap, but this may be too costly except in times of severe shortage, and there would be a 3-yr lead-time factor.

Maraging Steels (24)

Maraging steels (predominantly nickel, cobalt (7.5 to 12 pct), molybdenum, and titanium) had initial applications in ultra-high-strength materials with good toughness for use in the aerospace industry, but are now used for tools and other structural applications as well. A cobalt-free alloy containing more titanium than the original alloy was recently developed and shows properties consistent with those of the cobalt-bearing grade. Therefore, cobalt is not essential, but for aerospace applications, time-consuming and costly qualification testing would be required before substitution could be made.

Catalysts (24)

The catalytic activity of cobalt is utilized in several chemical and petroleum refining processes. Hydrotreating processes utilize 8 to 11 wt pct molybdenum and 1.5 to 3.5 wt pct cobalt (or molybdenum and nickel) on an alumina support to remove sulfur, nitrogen, and metals (typically vanadium and nickel) from various petroleum streams. As the fundamentals of catalysis are better understood, and the quantifiable physical and chemical characteristics can be better correlated with measures of performance, the same results will be obtainable with lower metals content. Molybdenum-nickel catalysts are widely used in a variety of hydrotreating processes and are more effective than molybdenum-cobalt catalysts for denitrification and hydrogen uptake, whereas molybdenum-cobalt shows higher desulfurization activity. A significant portion of molybdenum-cobalt catalytic applications could use nickel without any substantial process penalty. So far, reclaimers have taken out only molybdenum and vanadium from spent catalysts, but plants with the capability to recover essentially all the cobalt from any type of catalyst are envisioned. Refineries also are gradually increasing the practice of catalyst regeneration--cleaning up spent catalyst and returning it to useful life.

Hydroformylation reactions produce C_4 to C_{13} alcohols. C_4 to C_5 alcohols are used as solvents; the higher alcohols are further processed to produce plasticizers; some C_{12} alcohol is used to make detergents. The oxo process reacts ethylene or propylene with carbon monoxide and hydrogen over a cobalt catalyst (as a soluble salt) to form these linear alcohols. These alcohols are also available from the same process using a rhodium catalyst, as well as via an alternate route (Ziegler-type oligomerization) which uses catalysts other than cobalt. Oxo alcohol catalysts are recycled, but eventually buildup occurs on the process equipment, requiring that the material be reclaimed. About 90 pct of the cobalt is now being reclaimed, and the remainder is lost in handling.

Terephthalic acid and dimethylterephthalate are produced from paraxylene for use in the production of polyester fibers

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and films. The oxidation steps in the reaction are promoted by a cobalt-manganese catalyst. There does not appear to be a substitution alternative to cobalt in this process. There is recycling of the catalyst, but as byproducts build up, the catalyst is withdrawn and cobalt-containing sludge is incinerated and sent out for reclamation of cobalt. As a major user installs incineration facilities, the amount being reclaimed will increase to 90 pct.

Pyrolysis gasoline is the byproduct of the process used to make ethylene and propylene by thermal or steam cracking of hydrocarbon feedstocks. Pyrolysis gasoline is catalytically treated in two stages to saturate the olefins present and to remove sulfur; cobalt catalysts are used in the second stage. Nickel-molybdenum catalysts can also be used for pyrolysis gasoline processing. There is currently no reclamation of cobalt from pyrolysis gasoline catalysts.

The production of some organic acids also uses small quantities of cobalt catalysts. Acetic acid produced via high-pressure methanol carbonylation uses cobalt acetate and iodine as catalysts; adipic acid production uses cobalt naphthenate or stearate in the first oxidation step; benzoic acid production may also use a cobalt catalyst. Many other routes to organic acids are in commercial practice so the use of cobalt can be circumvented. The status of reclamation of organic acid catalysts is unknown.

Possibilities exist for increased use of cobalt catalysts in hydrotreating and shale oil processing, but it is possible to use nickel catalysts in place of cobalt in these processes with nearly equivalent results.

Paint Driers (24-25)

The role of cobalt in oil-base paint formulations is that of a catalytic agent surface drier. The drier is usually derived from cobalt metal reacted with an organic acid in water for chemical reactivity and dispersed in mineral spirits for physical solvency and convenient liquidity at concentrations of 6 to 24 pct Co. The function of the organic acid is to form a cobalt soap that is soluble in the diverse range of paint media with minimal concomitant detracting properties for the particular application. The drying process involves the conversion of the liquid to a solid by a chemical oxidation mechanism. Cobalt soap is usually preferred over manganese, cerium, iron, and zirconium soaps in the class of "top driers" in terms of speed of reduction and disappearance of surface tack, product discoloration, and durability. Top driers are complemented by "bottom driers" (usually soaps of lead, zinc, calcium, potassium, or zirconium) which hasten the solidification of the liquid coating down through the film to the substrate.

Cobalt is the most effective surface drier additive in oil-base paints. The amount of cobalt used is typically 0.05 pct (range 0.01 to 0.05 pct). To attain the same drying speed more manganese is usually needed, but this results in more discoloration and poorer durability. Iron has been used only where its inherent brown hue is acceptable. Cerium and zirconium have some favorable properties, but none is an alternative to replace cobalt directly on a one-to-one basis. Replacement is hampered not only by the complexity of the chemical mechanisms of paint formulation and degradation, but also by the vast diversity of types of paints. If cobalt were eliminated or reduced there would be attendant costs in convenience and product quality in most cases. The dissipative nature of the product obviously precludes reclamation.

Other Chemicals (24)

Pigments

Cobalt aluminate and silicate and associated oxides of other transition metals provide a range of violet, blue, and green inorganic pigments, with ultimate resistance to high heat, light, and bleeding (organic solubility), as well as special infrared reflectance. Military insignia and camouflage command high priorities for cobalt colors. With the exception of camouflage, all other

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uses could be considered nonessential; manganese and other transition metals are potential substitutes in several applications.

Ground-Coat Frit

Cobalt oxide (0.1 to 1 pct) is used by the porcelain enamel industry to enhance the adhesion onto metal of alkali alumino-borosilicate glasses, which are ground into frits. Cobalt-base frit is the preferred coating, but there has always been some nickel oxide used along with the cobalt oxide. The cobalt oxide component can be diminished and the nickel oxide component increased, but frits made with very low cobalt oxide content and high nickel content display inferior durability.

Glass Decolorizers

Cobalt is used to neutralize the coloring of impurities such as iron and chromium in an average glass batch. Cobalt is needed where glass has to be optically clear.

Miscellaneous

Accelerators and Stabilizers

The production of unsaturated polyesters for use in gel coats, laminates, and compression moldings utilizes a 12-pct cobalt octoate solution as a promoter to influence the time of cure and related properties. Gel coats and laminates have the more critical need for cobalt because they cure at ambient or slightly higher temperatures.

Animal Feeds

Cobalt has been used as a trace mineral diet additive in the United States for cattle, sheep, hogs, and poultry to enable the animals to generate vitamin B_{12} for increased growth.

Electronics

In electronics, soluble cobalt salts are used for magnetic audio and video tapes; cobalt oxide is used for varistors and thermistors.

Rubber Tires

In the manufacture of steel-belted radial tires, the presence of cobalt enhances the adherence of rubber to steel.

Battery Manufacturing

Cobalt imparts improved recharging characteristics to power cells and nickel-cadmium batteries.

Other Minor Chemical Uses

Cobalt chemicals are also used in small quantities in several other minor uses: electroplating and electrorefining, desiccant indicators, nucleating agents in investment casting, promoters in water treatment, chemical fuels, components in special oil drilling muds, etching tool steels, printing inks, and fertilizers.

Cobalt used as chemicals other than catalysts could be reduced by 20 pct without much difficulty. Further reductions could come from the rubber tire and battery sectors. However, some uses do require cobalt to accomplish the desired effect. Consumption of cobalt in the "miscellaneous" category could be reduced by 40 pct without serious consequences. Overall, a reduction of 60 pct could be achieved for "other chemicals."

SUPPLY ALTERNATIVES

Domestic (24, 29-30)

The Bureau of Mines has evaluated 24 domestic cobalt-bearing deposits with regard to the feasibility of cobalt recovery either as the principal product from sulfide or nickel-cobalt laterite occurrences, or as a byproduct of lead or copper. Six of these sites are active mines, all currently producing lead in Missouri, but no attempt is made to extract the cobalt contained in the ore; instead it is lost to the tailings and slag. Cobalt recovery would require the addition of another process circuit and incur added smelting and refining costs.

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Basically, the technology exists to produce primary cobalt from domestic sources, but the Bureau has concluded that higher prices (cobalt, $25/lb; copper, $1/lb; lead, $0.40/lb) are necessary to supply a significant percentage of U.S. cobalt consumption. Not only are the economics presently unattractive, but the time required to bring new domestic mines into production has been estimated at 5 yr or more. If circumstances eventually do favor cobalt production in the United States, two relatively high-grade deposits which have been mined for cobalt previously, the Blackbird Mine in Idaho and the Madison Mine in Missouri, are considered to be likely candidates for development (table 3), but intensive mining efforts would rapidly deplete these modest resources.

Despite current prices, California Nickel Corp. recently announced plans to build a demonstration plant in 1984 to extract nickel and cobalt from its nickel laterite deposit near Gasquet Mountain, CA. Construction of a commercial-scale plant is planned for 1987 (31). The U.S. Air Force, seeking to develop a secure source of cobalt suitable for use in making superalloys, has been considering requesting proposals for a pilot plant to process native cobalt ore (32). The only cobalt refinery in the United States at present is owned and operated by AMAX, Inc., in Louisiana with a capacity of 2 million lb of cobalt annually (33). The refinery treats foreign cobalt-containing nickel matte.

A Bureau research effort indicates that the heap-leaching method of recovering copper, which currently accounts for about 18 pct of U.S. copper production, may provide an opportunity for cobalt extraction. Passing the leach solutions through resin columns, washing with sulfuric acid, and extracting with solvent produces a concentrated cobalt solution. Further Bureau work will focus on the economic feasibility of the process (34).

Foreign (24, 30)

Cobalt is almost universally recovered as a byproduct of other mining and refining operations, so the potential for increasing cobalt output is ultimately limited by the economics of the metal of principal importance. The historic price levels of 1978-80 provided an incentive for increasing byproduct capacity, especially from nickel resources.

The copper mines of Zaire and Zambia remain the most important sources of world cobalt production, together providing about 60 pct of the total. Zaire possesses the richest cobalt ores in the world (0.3 to 0.5 pct). Zambian ore grades range from 0.1 to 0.2 pct, and accumulated copper smelter slags grade out at 0.6 pct, presenting another potential, although currently uneconomic, source of supply.

Most of the remaining cobalt production from market economy countries is a byproduct of nickel sulfide and laterite mining in Australia, Canada, the Philippines, Botswana, and New Caledonia; a great deal of New Caledonian cobalt is now lost because of the production process, which yields ferronickel. Some of the Canadian production is refined in Norway, while all of the cobalt from the other four sources is exported to Canada, Japan, France, or the United States for refining. Finland's cobalt production is derived from both copper and nickel sources, while the Republic of South Africa extracts some cobalt from platinum-group metal operations. Morocco had been producing cobalt as a principal product, but reserves there have been virtually depleted.

TABLE 3. - Principal U.S. cobalt resources

Location	Owner and/or operator	Ore grade, pct
Blackbird Mine, Idaho.	Hanna Mining Co., Noranda Exploration Inc.	0.55
Madison Mine, Missouri.	Anschutz Uranium Corp.	.25

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Nickel sulfide ores currently represent the major source of cobalt from which production could be increased in the near future, but the large cobalt resources in nickel laterites, occurring mainly in New Caledonia, Indonesia, the Philippines, and Cuba, could eventually become the most important land-based source of cobalt. Of all the North American cobalt resources, Canadian nickel deposits have the greatest potential for being competitive alternatives to existing cobalt supply sources.

Ocean Minerals (24)

Deep-sea manganese nodules typically contain 0.1 to 0.5 pct Co. Marine manganese crusts, some containing perhaps 1 pct Co at relatively shallow depths (less than 2,500 m), have been located in the Pacific Ocean south of Hawaii, and in the Atlantic Ocean off the southeastern shore line of the United States. Assessments of these occurrences are in progress. The current impediments to ocean mining have been discussed previously.

Stockpile (30)

In 1981 the General Services Administration (GSA) purchased 5.2 million lb of cobalt from Zaire for the National Defense Stockpile. By yearend 1982 delivery was completed. In 1983 GSA purchased 6.5 million lb of cobalt for the stockpile, with delivery expected to begin early in 1984. Zaire will supply 4 million lb and Zambia the remainder, all at $5.50/lb. GSA awarded a contract for an additional 0.5 million lb at $11.70/lb to Inco, Ltd., of Canada in 1984 (35).

A panel of industry experts assembled by the American Society for Metals at the request of the Federal Emergency Management Agency determined that the recently acquired cobalt meets the quality requirements of current technology for the most critical defense and industrial applications, but the present condition of the cobalt purchased during 1947-61 precludes its use for producing vacuum-processed alloys. However, domestic capability (process and equipment) exists to upgrade the quality of the pre-1980 cobalt (36).

SUMMARY OF DEMAND AND SUPPLY ALTERNATIVES

The price increases of 1978 caused a substantial reduction in the amount of cobalt used in applications where economic alternatives were readily available. Another round of high prices would lead to further substitution, but not with the facility experienced previously.

Current essential U.S. cobalt needs are estimated at about 50 pct of present consumption. Existing substitution, processing, recycling, and design technology is capable of achieving cobalt savings of over 10 million lb annually by the next decade, based on an estimated consumption level of 22 million lb.

Significant amounts of cobalt in superalloys could be replaced, but this would require costly and time-consuming alloy optimization and engine certification programs.

A great deal of substitution for cobalt in magnetic applications has already occurred. An estimated 20 pct of current cobalt use in these applications is essential and would continue at even a tenfold price increase.

Cobalt is a key requirement for cemented carbides, which are critical to high productivity in metal cutting and forming, mining, oil and gas well drilling, and other industrial operations. Cobalt-free materials cannot be considered as practical general alternatives.

In wear-resistant applications cobalt is required only for protection against galling and cavitation erosion, and even for these uses lower cobalt substitutes will suffice.

Cobalt-free grades of high-speed tool steels and maraging steels have been developed.

Hydrotreating is the catalytic process most amenable to substitution by cobalt-free materials.

Cobalt is the single most effective surface drier additive in oil-base paints. Elimination or reduction of cobalt would incur substantial penalties in convenience and product quality.

A 60-pct reduction in the amount of cobalt used in other chemical applications could be accomplished.

Most in-house and prompt industrial scrap is recycled, and cobalt is generally recovered.

Obsolete, low-grade, and mixed alloy scrap is not efficiently recycled. Some better quality obsolete scrap is recycled for superalloys, but a large quantity is downgraded. Most low-grade scrap (dusts, mill scale, grindings) is downgraded also, and its cobalt content is lost. Treatment of mixed-alloy scrap to recover all contained elements is technically feasible but not economically practicable.

Near-net-shape technologies can achieve improved yield of usable product from raw materials.

Zaire and Zambia should continue to be the dominant suppliers in the world cobalt market.

The technology exists to produce cobalt metal from domestic deposits, but total production costs would be at least $20/lb to $25/lb, and the time required would be at least 5 yr.

Of all the potential North American cobalt resources, Canadian nickel deposits have the greatest potential of being competitive alternatives to existing cobalt supply sources.

CHROMIUM

BACKGROUND

The uses of chromium encompass three major areas--metallurgical (as an alloying element that imparts a variety of important properties to many ferrous and nonferrous alloys, principally stainless and full-alloy steels), refractory (chromite refractory bricks to line metallurgical furnaces, glass regenerators, and rotary kilns), and chemical (mainly pigments, plating, and leather tanning). Tables 4 and 5 quantify these uses. Production of chromite ore in the United States ceased after 1961 (except for a small amount produced for export in 1976), and at present, domestic chromite resources are considered to be uneconomic to develop. Therefore, all chromite consumed in the United States is imported, mainly from the Republic of South Africa and the Philippines. Historically chromite has been classified into three general grades associated with the major end-use categories, but considerable interchangeability among the grades has evolved. Current nomenclature reflects the composition of the ore (high-chromium, high-aluminum, high-iron) rather than end use.

In addition to chromite, substantial quantities of chromium are also imported as ferroalloys, predominantly high-carbon ferrochromium, which is the typical form used to add primary chromium to steel. World ferroalloy production capacity has been shifting to ore-producing countries. As a result, imported chromium ferroalloys have been steadily increasing their share of total chromium imports relative to chromite, and of total U.S. chromium ferroalloy supply at the expense of domestic production (table 6), a trend which threatens the viability of the U.S. ferroalloy industry.

TABLE 4. - U.S. consumption of chromite, by primary industry

Industry	1981		1982		1983	
	Gross weight, 10^3 st	Average Cr_2O_3, pct	Gross weight, 10^3 st	Average Cr_2O_3, pct	Gross weight, 10^3 st	Average Cr_2O_3, pct
Metallurgical.....	503	35.7	270	35.1	64	39.3
Refractory.....	148	37.3	80	36.4	72	36.9
Chemical.....	238	42.6	195	44.9	189	44.7
Total.....	889	37.9	545	38.8	325	41.9

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TABLE 5. - U.S. consumption of chromium ferroalloys and metal, by end use

(Thousand short tons, gross weight)

End use	Ferrochromium	Ferrochromium silicon	Metal and other	Total[1]
1981				
Carbon steel	8	1	(2)	9
Stainless and heat-resisting steel	287	14	(2)	302
Full-alloy steel	71	4	3	79
High-strength low-alloy and electric steel	7	2	3	12
Tool steel	4	(2)	0	5
Cast iron	10	(2)	1	11
Superalloys	7	W	2	9
Welding materials (structural and hardfacing)	2	0	(2)	2
Other alloys	2	(2)	2	4
Miscellaneous	2	(2)	(2)	3
Total[1]	400	22	11	434
Chromium content	238	8	7	253
1982				
Carbon steel	6	1	(2)	6
Stainless and heat-resisting steel	181	10	(2)	191
Full-alloy steel	37	3	1	41
High-strength low-alloy and electric steel	5	2	1	8
Tool steel	2	(2)	0	2
Cast iron	7	(2)	(2)	7
Superalloys	6	(2)	2	8
Welding materials (structural and hardfacing)	1	W	(2)	1
Other alloys	1	(2)	1	2
Miscellaneous	1	(2)	(2)	1
Total[1]	247	15	7	268
Chromium content	147	5	5	157
1983				
Carbon steel	7	(2)	0	8
Stainless and heat-resisting steel	305	12	(2)	318
Full-alloy steel	33	2	(2)	34
High-strength low-alloy and electric steel	5	2	(2)	7
Tool steel	4	W	(2)	4
Cast iron	6	(2)	(2)	6
Superalloys	7	W	3	10
Welding materials (structural and hardfacing)	1	W	(2)	1
Other alloys	2	(2)	1	3
Miscellaneous	1	(2)	(2)	2
Total[1]	371	16	5	392
Chromium content	219	6	4	229

W Withheld to avoid disclosing company proprietary data; included with Miscellaneous.

[1]Data may not add to totals shown because of independent rounding.

[2]Less than 1/2 unit.

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TABLE 6. - Domestic production and imports of chromium ferroalloys and chromite

(Thousand short tons)

Year	Chromium ferroalloys[1]				Chromite: Imports		
	Domestic production		Imports		Gross weight	Cr_2O_3 content	Chromium content
	Gross weight	Chromium content	Gross weight	Chromium content			
1963.....	300	180	30	21	1,391	605	414
1973.....	418	260	180	113	931	412	282
1981.....	226	127	443	255	898	368	252
1982.....	119	69	150	89	507	209	143
1983.....	36	19	285	167	190	86	59

[1]Includes high- and low-carbon ferrochromium, ferrochromium-silicon, and chromium metal.

Calculated apparent consumption of chromium in all forms was 329,000 st in 1983. This represented only a slight increase over the 1982 total, which was the lowest amount since the 1950's, basically reflecting the recent performance of the steel industry. Chromium demand attained its highest level in 1974 at 625,000 st. In 1983 prices for chromite (f.o.b.) were $48/mt to $52/mt from the Republic of South Africa and $110/mt from Turkey; the price of imported 50- to 55-pct high-carbon ferrochromium ranged from $0.355/lb to $0.40/lb. Total domestic chromium demand is forecast to grow at an average annual rate of 2.2 pct from 1981 to 2000. Table 7 contains world production and reserves of chromite, and chromium imports by the United States, as ore and ferrochromium.

USES AND DEMAND ALTERNATIVES

Metallurgical

Prior to identifying the specific substitution and surface modification methods that can save chromium, the conservation role of modern steel-making process technologies and novel metallurgical techniques also should be examined (18, 25-26, 37-40).

Although continuous casting is well established, opportunities exist for further application. The process results in significantly higher product yields, improved product quality, and cost advantages over ingot casting. Use of continuous casting in conjunction with the argon-oxygen decarburization (AOD) process has been credited with improving chromium yield in stainless steels by 10 to 15 pct. AOD uses the furnace for melting only--a separate vessel accommodates decarburization and refining. Oxygen and argon are introduced to oxidize and remove carbon, thus achieving low carbon content while minimizing the oxidation of chromium and other elements and subsequent loss to slag. This greatly reduces the need for additions of low-carbon ferrochromium to obtain the desired composition, permits the use of cheaper raw materials (high-carbon ferrochromium, more scrap), and results in lower costs for energy (because of reduced operating temperatures).

Wider application of duplex refining systems, some utilizing special melting and remelting techniques, appears to be a promising means of achieving substantial conservation of chromium. Cost-competitive steels that possess properties comparable or superior to those of traditional steels can be produced without using large amounts of alloying elements or elaborate heat treatment. This requires an understanding of the specific influence of the various fabrication-process variables on steel microstructure and the resultant properties that can be predicted.

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TABLE 7. - World chromite mine production, reserves, and U.S. imports

(Thousand short tons)

Country	Mine output			Reserves[1]	U.S. imports					
					Chromite[2]			Ferrochromium[3]		
	1981	1982[p]	1983[e]		1981	1982	1983	1981	1982	1983
Albania	937	965	990	2,000	14	4	6	0	0	4
Belgium	0	0	0	0	0	0	0	(4)	0	(4)
Brazil	260	304	310	9,000	0	0	0	21	17	8
Canada	0	0	0	0	0	0	6	0	(4)	(4)
China	0	0	0	0	0	0	0	3	6	0
Cuba	23	30	35	NA	0	0	0	0	0	0
Cyprus	11	11	11	1,000	0	0	0	0	0	0
Finland	454	380	375	19,000	78	45	0	0	0	0
France	0	0	0	0	0	0	0	2	0	(4)
Germany, Federal Republic of	0	0	0	0	0	0	0	5	4	2
Greece	47	46	45	NA	0	0	0	0	0	0
India	369	374	400	15,000	0	0	0	0	0	0
Iran	35	45	55	4,000	0	0	0	0	0	0
Italy	0	0	0	0	0	0	0	1	(4)	(4)
Japan	12	12	9	NA	0	0	0	1	(4)	2
Korea, Republic of	0	0	0	0	0	0	0	0	0	1
Madagascar	110	100	100	NA	18	41	21	0	0	0
New Caledonia	4	55	100	2,000	0	0	0	0	0	0
New Guinea	0	0	0	0	(4)	0	0	0	0	0
Norway	0	0	0	0	0	0	0	2	(4)	1
Pakistan	1	1	1	1,000	0	3	0	0	0	0
Philippines	484	391	365	23,000	145	70	13	2	(4)	0
South Africa, Republic of	3,164	2,385	2,460	910,000	482	277	144	261	55	152
Spain	0	0	0	0	0	0	0	1	0	(4)
Sudan	29	28	30	NA	0	0	0	0	0	0
Sweden	0	0	0	0	0	0	0	11	4	11
Turkey	466	448	440	5,000	49	32	0	8	6	15
U.S.S.R.	2,646	2,701	2,700	17,000	111	34	(4)	0	0	0
United Kingdom	0	0	0	0	0	0	0	0	(4)	(4)
Vietnam	17	18	20	NA	0	0	0	0	0	0
Yugoslavia	(4)	0	0	NA	0	0	0	47	16	33
Zimbabwe	591	476	475	19,000	0	0	0	62	33	53
Total	9,660	8,770	8,921	[5]1,000,000	898	507	190	428	141	280

[e]Estimated.
[p]Preliminary.
NA Not available.
[1]Shipping-grade ore (deposit quantity and grade normalized to 45 pct Cr_2O_3 for high-chromium and high-iron chromite; 35 pct Cr_2O_3 for high-alumina chromite).
[2]Average Cr_2O_3 content: 1981--41.0 pct, 1982--41.2 pct, 1983--45.3 pct.
[3]Average chromium content: 1981--57.8 pct, 1982--60.0 pct, 1983--58.2 pct.
[4]Less than 1/2 unit.
[5]Rounded.

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Powder metallurgy also offers possibilities for chromium conservation. The use of powder formed by rapid solidification enables production of alloys with unique microstructures, and therefore, with properties not attainable with conventional metallurgical techniques. Near-net-shape technology minimizes material and energy use through reduced scrap generation.

Stainless Steels (18, 25-26, 37-40)

The largest use for chromium is the production of stainless and heat-resisting steels. Stainless steels actually are defined by their chromium content. Austenitic stainless steels constitute about 70 pct of U.S. stainless steel production, generally contain 17 to 36 pct Cr, and are used for many industrial processing, energy generation, pollution control, cryogenic, marine, transportation, construction, and consumer product applications; martensitic stainless steels account for about 25 pct of domestic production, usually contain 11.5 to 18 pct Cr, and are used as a lower cost alternative to austenitic types in surgical instruments and some intermediate-temperature and oil industry applications; ferritic stainless steels average slightly higher chromium contents than martensitic types, but are used mostly for decorative purposes. Heat-resisting steels usually are included with stainless steels although they contain only 4 to 10 pct Cr; they can be substituted for stainless steels in certain instances.

Chromium provides passivation in iron-base alloys, and a minimum of about 12 pct Cr is required for this purpose. Additional chromium increases the resistance of iron-base alloys to corrosion and oxidation by various degrees. Another function of chromium in austenitic stainless steels is to stabilize the structure. Because chromium has been a readily available, low-cost element, and because some higher chromium steels offer outstanding fabricating characteristics, stainless steels have been designed into a large number of applications. Chromium savings could be accomplished by partially replacing the chromium in excess of 12 pct with other alloying elements, by completely replacing stainless steel with a different material containing little or no chromium, by employing thinner gauge or longer lasting high-chromium alloys, or by using surface modification techniques, so that the properties of chromium are utilized only where they are needed. Nevertheless, changes require careful evaluation of the service requirements for the particular application.

Steels possessing lower chromium content provide the least chromium savings, but their mechanical and fabricating characteristics can more closely approximate those of the standard stainless steels. The loss in corrosion and oxidation resistance caused by the lower chromium content can be partly or completely compensated for by the addition of other alloying elements:

1. For most applications 12 pct Cr will provide corrosion resistance. The function of chromium as an austenite stabilizer can be performed as effectively by manganese or nickel. In many chemical processes, however, the use of 12 pct Cr requires additions of molybdenum, silicon, or aluminum to attain the corrosion resistance of type 304 stainless steel (the most widely used grade).

2. Austenitic stainless steels with about 14 pct Cr appear to have adequate strength and oxidation resistance for service up to 1,400° F.

3. A composition of 12 pct Cr with silicon, aluminum, and nickel additions has corrosion resistance in aqueous environment and oxidation resistance in air superior to those of type 304 stainless steel.

4. A 9Cr-1Mo steel, modified by small additions of columbium and vanadium, is being tested as a replacement for 18-pct-Cr steels in steam powerplant heat exchangers. A 9Cr austenitic stainless steel with molybdenum and possibly copper and vanadium, having corrosion resistance comparable to that of standard grades except in severe environments, appears feasible.

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5. Modified 6-pct-Cr steels appear to be promising replacements for the 12-pct-Cr type in automotive emission control systems.

6. High-strength duplex stainless steels and corrosion-resistant superferritic stainless steels contain as much or more chromium than standard types, but afford reduced cross-section dimensions and less frequent replacement of components.

Several no-chromium alternatives are in use or under development:

1. Iron-manganese-aluminum alloys are being developed as potential substitutes for austenitic stainless steel grades in heat-resistant applications at moderate temperatures and some corrosion-resistant applications. Although brittle, they have been successfully used in furnace and ocean environments.

2. Aluminum steels such as Fe-8Al-6Mo have demonstrated high-temperature oxidation resistance in air superior to that of type 304 stainless.

3. High-silicon (9 to 18 pct) alloys of iron, cobalt, or nickel offer excellent resistance to corrosion but need improvement with regard to mechanical properties and fabrication. Smaller (1 to 4 pct) additions of silicon are sufficient to enhance oxidation resistance.

4. Silicon-molybdenum ductile iron has performed more effectively than high-chromium steels in high-temperature corrosive and/or erosive environments such as furnace grates and auto exhaust manifolds. This material is a possible alternative to high-chromium steels in numerous high-temperature applications.

5. Nickel-copper and nickel-molybdenum alloys may also be used for corrosion resistance with some sacrifice of performance and mechanical properties.

6. Metals such as titanium (seawater exposure, chemical apparatus), tantalum (chemical apparatus), aluminum, nickel, platinum, zinc, and zirconium, and nonmetallic materials such as glass (excellent resistance to corrosive chemicals), graphite (high strength), ceramics, and plastics have proven records in a number of specialized functional and decorative applications. In most cases larger scale use is limited mainly by costs, availability, and complexities concerning fabrication and installation, but increased use of plastics appears to be a viable alternative to stainless steel, particularly where elevated-temperature service is not a factor. Plastics such as polyethylene, Teflon, and polyurethane have excellent resistance to corrosive chemicals and are readily fabricated into plant equipment. Glass mat or fiber reinforcement provides some strength and extends applicability.

Surface protection via cladding and coating techniques is an additional option that can be used to prevent corrosion, oxidation, and wear. This approach also offers the opportunity for considerable reductions in the use of chromium-containing stainless steels:

1. Cladding technology is well established. Individual strips of metal are passed through a pressure rolling mill to merge the lattices of the metals into a common structure; subsequent thermal treatment promotes diffusion, improves bond strength, and provides cold-work stress relief. Most active metals and alloys can be clad. Stainless-clad carbon steels are used extensively in the chemical process industries for large columns and vessels. The initial cost is lower than for solid stainless, but usage is limited to configurations that can be made from sheet and plate, specialized joining techniques must be employed, and edges must be protected. Additional usage is technically feasible but uneconomic at present. Cladding base steels with metals other than stainless steel could achieve even greater chromium savings.

2. In contrast to wrought metal cladding, electroplating can be employed to obtain a chromium coating. Fabricated parts, brittle materials, and selected areas can be electroplated, but the major limitation is the size and shape of a component that can be plated. Chromium-rich diffusion coatings have been shown to be more widely applicable than electroplating, but item size and shape limitations also exist, as well as the requirement for high-temperature processing.

3. Directed energy beam techniques (ion beam processing, laser beam processing) can produce chromium-containing coatings which are metallurgically bonded to the surface with performance comparable to or better than that of bulk chromium alloys. Since a vacuum or helium atmosphere is required, the substrate is limited in terms of size, and it must also be open and recess-free.

4. The oxygen-diffused nitriding process (salt bath treating) has the capability of producing a surface comparable or superior to that with chromium plating with respect to corrosion and wear resistance in many applications at similar cost. In addition, the discharge of none of the compounds present in the system effluent is restricted.

5. Electroless nickel is an amorphous nickel and phosphorus coating applied via autocatalytic chemical reduction. It offers high strength, excellent abrasion, wear, and corrosion resistance (in most environments the corrosion resistance of hard chromium is much less), uniform thickness, solderability, and ease of application. The petroleum and chemical process industries are the principal users of electroless nickel coatings.

6. Some corrosion-resistant materials, such as elastomers and lead, are limited to specialized lining applications. Their lack of strength must be compensated for by the structural capabilities of the basis material. Polymer concrete (concrete in which aggregate is bound in a dense matrix with a polymer binder) has demonstrated its utility as a liner for carbon steel exposed to corrosive geothermal brines, which chemically attack most conventional construction materials. Polymer concrete also offers a 10- to 20-pct cost reduction.

Changes to less exotic chemical-process equipment can be made in some circumstances through modifications to process chemistry by using inhibitors, making minor changes in the process stream, and eliminating contaminants.

Stainless steel scrap is the major source of secondary chromium supply. Home scrap generated in the production process is retained and reused. Prompt industrial scrap can also be recycled effectively if properly segregated, particularly the stainless steels containing other high-value alloy metals. An operation in Pennsylvania even recovers chromium and nickel in the form of remelt alloy from plant particulate wastes, such as dusts, mill scale, and grinding swarf. Although there is considerable chromium in the waste products of some other metallurgical industry processes, collection and processing costs hinder economical recovery on a large scale (except for superalloys). The Bureau of Mines is actively developing recycling technology in these areas (41). Much obsolete stainless steel scrap is downgraded or not recovered. Scrapped automobiles, particularly the catalytic converter canister, represent a large source of available chromium.

Alloy Steels (18, 25-26, 37-40)

After stainless steels, the next largest metallurgical consumer of chromium is alloy steels, which owe their enhanced properties to a specified alloy content, often some combination of chromium, molybdenum, and/or nickel. Chromium influences hardenability--the property of a steel that determines the depth and distribution of hardness that may be induced by quenching--and can be present up to 1.7 pct. Alloy steels are used in structural engineering, machinery, and transportation equipment. Common AISI grades of these steels are the chromium-molybdenum 4100 series such as 4130 and 4140, containing 0.8 to 1.1 pct Cr and used for fittings, valves, bolts, shafts, teeth, etc.; the nickel-chromium-molybdenum 8600 and 8700 series such as 8620 with 0.4 to 0.6 pct Cr, for use in gears; and the straight chromium 5100 series such as 5160 containing 0.7 to 0.9 pct Cr, used in coil and leaf springs.

Historically, the basis for alternative alloy steels has been that of achieving equivalent hardenability as exemplified by the development of the National Emergency Steels during World War II, and the SAE EX steels during the Canadian mining strike and subsequent nickel shortage in

1969-70. In the last several years computerized hardenability prediction systems have provided a rapid and highly accurate means of predicting the properties of a steel as a function of composition, thus offering the opportunity to design substitute alloys in less time by avoiding a lengthy program of melting and evaluating experimental compositions. (Two chromium-free steels, a manganese-molybdenum grade and a manganese-nickel-molybdenum grade, have been computer-designed under Bureau of Mines contract to be equivalent to the AISI 8600 and 4100 steels.) While the use of chromium is highly efficient, many opportunities exist to eliminate or reduce the chromium content of these steels by using other alloying elements that also have a strong influence on hardenability, although in most areas the addition of these substitute elements carries an economic penalty relative to current chromium prices.

The most commonly used carburizing steels contain 0.5 to 1 pct Cr for case and core hardenability, but several standard chromium-free alternatives are available, usually with increased amounts of manganese and/or molybdenum.

Through-hardening grades normally contain 0.5 to 1.5 pct Cr for hardenability and toughness, but manganese, molybdenum, boron, and silicon levels can be adjusted to produce chromium-free substitutes.

Constructional alloy plate steels, used for bridges and other structures, have adequate chromium-free alternatives available, usually with higher molybdenum and boron content.

Abrasion-resistant plate steels also have varieties without chromium, such as carbon-manganese, carbon-manganese-molybdenum-boron, and carbon-manganese-molybdenum-nickel-boron quenched and tempered alloys.

Weathering plate steels, used in welded bridges and in buildings where weight savings and durability are required, usually contain chromium, but some chromium-free types are available with increased nickel and copper levels.

Low-alloy constructional cast steels have an average chromium content of 0.7 pct, which can be adequately substituted for by increasing the levels of one or more other alloying elements such as manganese, nickel, molybdenum, or boron.

Spring steels (0.7 to 0.9 pct Cr) and grinding mill ball steels (0.45 pct Cr) have chromium-free alternatives available.

An alternative bearing steel with 0.4 to 0.6 pct Cr offers superior processing and performance characteristics at lower cost compared with high-carbon grades containing 1.3 to 1.6 pct Cr.

Ultra-high-strength steels are used principally in load-bearing aircraft forging applications that require high strength and good fatigue resistance. These steels all contain chromium (0.8 to 1 pct), and no known chromium-free substitute alloys are available. Likewise, no substitutes are available for existing pressure vessel plate steels (0.5 to 2 pct Cr to provide corrosion resistance).

Many different heat treatments are used to enhance the engineering properties of steel. Induction heating provides high energy density for controlled depth heating, reducing the amount of heat that must be removed in the quenching process. Selective use can reduce or eliminate the need for hardenability-enhancing alloys in heat treating engineering steels. Applications other than hardening, such as induction treatment to provide corrosion resistance, have been demonstrated experimentally.

High-strength low-alloy (HSLA) steels generally do not contain chromium. Their scope could be extended to include areas reserved for heat-treatable chromium-containing steels.

High-Strength Low-Alloy Steels (38-39, 42-43)

High-strength low-alloy (HSLA) steels constitute a separate class of steels with high yield strength and good toughness, formability, and weldability. These properties are achieved by using micro additions (less than 0.1 pct) of key alloying elements (most commonly columbium, vanadium, and titanium) and controlled thermomechanical treatments. In some cases, other alloying elements, such

as molybdenum, nickel, and chromium, are also added, but the majority of HSLA steels do not contain chromium.

Conventional low-alloy steels, containing varying amounts of molybdenum, nickel, and chromium, can attain equivalent or greater yield strengths, but they require heat treatment and their higher carbon contents adversely affect toughness and weldability. Since HSLA steels achieve their strength without an increase (and usually with a substantial decrease) in carbon content, properties other than strength are preserved.

HSLA steels have been used predominantly to meet a combination of requirements in pipeline service and for fuel-saving weight reductions in the automotive industry. HSLA steels are becoming available in an increasing number of forms for a variety of applications, including possible displacement of chromium-containing heat treatable steels.

Tool Steels (18, 25, 37)

The chromium content of tool steels ranges from 0.25 to 12.5 pct, but most contain 3 to 5 pct Cr. However, the total amount of chromium used in tool steels is small. The major use is in high-speed steels (cutting tools, hot-work dies), in which chromium plays an important role in the hardening mechanism. In the high-carbon, high-chromium, cold-work steels (blanking, forming, drawing, and slitting tools), chromium is essential for hardness and wear resistance. Sintered carbides perform adequately as substitutes in most cases (78 pct) for these two types, but serious cost penalties are incurred. Replacement of chromium hot-work steels (dies forging, molding, and extrusion tooling) is not feasible, and present technology does not indicate the development of chromium-free substitutes. Some of the other tool steels can be replaced by lower chromium steels or chromium-free materials, but the quantity of chromium involved is negligible.

Alloy Cast Irons (18, 37)

Indefinite chill rolls with chromium contents of 1.5 to 2 pct are interchangeable with cast steel rolls with less than 1 pct Cr or with spheroidal graphite rolls containing 0.4 pct Mo and no chromium. However, if these substitutions were made, roll performance in the mills would probably be reduced.

Alternatives to abrasion-resistant cast irons, containing 15 to 28 pct Cr for abrasion and impact resistance, include NiHard type 2 (1.5 to 2 pct Cr), NiHard type 4 (6 to 8 pct Cr), wrought low-alloy steels, and chromium-molybdenum pearlitic or oil-quenched and tempered steels containing less than 2 pct Cr. Alloy combinations of manganese, boron, tellurium, molybdenum, and tungsten could also be considered as chromium replacements.

Engineering castings contain 0.5 to 2 pct Cr for wear resistance, strength, and dimensional stability in transportation applications. The trend in smaller section sizes is toward irons with less or no chromium, such as tin-molybdenum and copper-molybdenum irons.

Superalloys (18, 25-26, 37, 39)

Typically, wrought nickel-base and iron-nickel-base superalloys contain 15 to 20 pct Cr; cast nickel-base, 10 to 15 pct; and cobalt-base, 20 to 30 pct. The presence of chromium is essential in superalloys to provide the resistance to oxidation and hot corrosion required for gas turbine engines. However, the high chromium content is needed only at the surface, not for the mechanical properties of the material. Ion implantation and laser annealing show the most promise to achieve the surface requirement for chromium while eliminating it from the bulk of the alloy.

Scrap recycling technology is pursued in the superalloy field because of the relatively high value of these materials (44).

Other Alloys (18, 37)

In alloys of aluminum, titanium, and copper, chromium is used primarily to control microstructure and improve physical and mechanical properties, but substitutes for chromium are readily available.

Aluminum-Base Alloys

Chromium is used as a minor alloying addition in many of these high-performance wrought alloys which are used in a variety of aerospace, marine, and surface vehicle load-bearing applications. The chromium alloying additions control recrystallization behavior, help achieve consistent product performance, and improve resistance to stress corrosion cracking. Zirconium and manganese produce effects that are similar to those produced by chromium, and replacement of the alloys containing chromium with chromium-free grades is possible in many applications. However, the slight performance penalties involved could be important in some critical structural uses. Also of concern are the lead time and expense involved in qualifying materials for aerospace applications.

Titanium-Base Alloys

Chromium is used as an alloying addition (2 to 11 pct) in several commercially available titanium alloys. Chromium serves to stabilize the high-temperature beta allotrope of titanium. Other elements (molybdenum, vanadium) also produce similar effects and are frequently used instead of or in combination with chromium. Therefore, chromium-free alloys are available with similar characteristics.

Copper-Base Alloys

Chromium additions (about 1 pct) produce useful strengthening effects in copper alloys but do not exhibit particularly unique property combinations. Apparently chromium-free grades could be substituted without significant cost or performance penalties.

Refractory (18, 37-39, 45-46)--Chromite Refractories

Chromite in the mineral (spinel) form imparts thermal shock and slag resistance, volume stability, and structural strength in refractories that range from all chromite to various mixtures of chromite and magnesia. They are designated as chrome (essentially all chromite), chrome magnesite (chromite equal to or greater than the weight percent of magnesite), and magnesite chrome (greater than 50 wt pct magnesite). Refractories are supplied as granular material or shaped brick. The two major uses of chromite in granular form are as maintenance gunning mixtures for steelmaking furnaces and as facing sands in steel foundries. Substitute gunning materials include magnesite, dolomite, salvaged and reprocessed chromite, and chromium-free basic materials. Substitute materials for facing sands include zircon, olivine, and silicon sands. Olivine is preferred for high-manganese steel castings. Silica sands are primarily used as backup, not facing, sands. The brick may be bonded chemically (unburned), burned, or fusion cast.

The steel industry is the predominant consumer of chrome-bearing refractories. However, chrome ore usage appears significantly less critical now than just a few years ago. The consumption of these refractories has been on a downward trend because of the continuing decline in open-hearth furnace steelmaking, which has been the principal user of chromite (table 8). The main replacement for the open-hearth process--the basic oxygen converter--uses refractories based only on periclase (MgO) with carbon. The other alternative, the electric furnace, does utilize chromite, but in the past

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TABLE 8. - Steel production in the United States, by type of furnace

(Percent)

Year	Open hearth	Basic oxygen converter	Electric
1963....	81	8	10
1973....	26	55	18
1981....	11	61	28
1982....	8	61	31
1983....	7	62	31

[1]Bessemer furnace production: 1 pct.

several years the extensive application of water-cooled sidewall panels and roofs has reduced the need for chromite by 60 to 70 pct. Most electric furnaces use brick made of periclase with carbon or graphite in the bottom, slag line, and interval from the slag line to the lower edge of the water-cooled panels. It is estimated that about 60 pct of installed electric furnace capacity in the United States is now water cooled, a practice that should steadily increase. Argon-oxygen decarburization and vacuum oxygen decarburization employ periclase-chrome or dolomite refractories. Apparently dolomite is capable of totally replacing periclase-chrome in this application.

Increased demand for higher quality steels has led to changes in ladle metallurgy and increased use of degassers and related processes, with a resulting preference for chrome refractory usage. Ladles are increasingly lined with periclase-chrome or other materials rather than fireclay, and degassers are conventionally lined with periclase-chrome and alumina refractories.

Glass, nonferrous, and rotary kilns also utilize chromite. For copper converters, higher chromium compositions reportedly give better performance. In most other applications, substitution of magnesite chrome for chrome and chrome magnesite can be made at no penalty in performance and minimal increase in initial cost. The extent of such substitution could yield a savings in chromite consumption for brick well in excess of 50 pct.

Considerable potential exists for salvage and reuse of chromium-bearing brick in all consuming industries (18, 47-49). Chromium-bearing bricks in many units are distinctly different and recognizable from chromium-free refractories even after use, so the bricks can be separated by hand and stacked separately for salvage, reprocessing, and reuse. Up to 33 pct of the bricks in an original steel-producing structure can be salvaged by such practice.

Chemicals (18, 37)

Chemical-grade chromite ore is roasted with soda ash and lime to convert the Cr_2O_3 to Na_2CrO_4. This is leached with water to extract the soluble sodium chromate. Sodium chromate is acidified with sulfuric acid or carbon dioxide to produce the principal chromium chemical, sodium dichromate. Most chromium chemicals are made from sodium dichromate.

In 1982, the Environmental Protection Agency set out its final regulations in accordance with the Clean Water Act on pollutants discharged in wastewater from inorganic chemical plants. Included in regulation coverage are chrome pigments and sodium dichromate. The Bureau of Mines is developing process technologies for reducing chromium losses in certain chemical operations (50).

Pigments and Paints

The main chrome pigments are chrome yellow, molybdenum orange, zinc chromate, chrome green, and chrome oxide green. The primary uses for chrome pigments are for coloring plastics, for printing inks, and in paints for highway lines and industrial finishes (vehicles, equipment, appliances). Zinc chromate is used mainly as a corrosion inhibitor primer for metals. Replacement of chromium pigments with proven nonchromium pigments to obtain the same color would involve a substantial price penalty. The chrome pigments could be replaced by pigments such as carbon black, iron oxide, and titanium

oxide, but these substitutes would limit the number of colors.

Leather Tanning

Chromium compounds are used to tan the bulk of the leather produced in the United States. Substitutes such as vegetable tanning compounds exact definite price and performance penalties.

Metal Finishing and Treatment

Chromium is used for chromium plating (decorative and engineering) and the treatment of copper, brass, zinc, and cadmium alloys, and galvanized steel. About 60 pct of the chromium consumed in electroplating is used in decorative end uses, 30 pct is used in engineering (hard) chromium plating, and the rest in other forms of metal finishing (chromate conversion coatings, chromic acid anodizing of aluminum). Obviously, decorative chromium plating could be discontinued--materials now being plated could be painted or made from chromium-free materials such as plastics. Hard chromium plating is used for its excellent physical properties, hardness, wear resistance, and low coefficient of friction. The only apparent substitute is electroless nickel, which is better than hard chromium for wear resistance in certain applications. In addition, its "throwing power" is far superior, and it does not degrade the fatigue properties as hard chromium plating sometimes does. Another use for chromium plating is in the manufacture of "tin-free steel" that can replace tinplate in some canning uses. Only 15 to 20 pct of the chromic acid used actually ends up on the plate, and a considerable saving of chromium can be accomplished by recycling the wasted material. Plating baths using trivalent chromium compounds in place of chromic acid would also yield savings from the use of less chromic acid spray and effluent.

Drilling Mud Additives

Sodium dichromate is used to produce chromium lignosulfonates for drilling muds; no satisfactory substitutes exist, especially for drilling deep wells (over 10,000 ft). Chromium compounds also are used as a corrosion inhibitor in additives to drilling muds to greatly extend the life of the drilling equipment.

Water Treatment Compounds

Sodium dichromate is used to make water treatment compounds such as corrosion inhibitors for cooling towers and air conditioners. The largest users are petrochemical and chemical plants and oil refineries. No substitutes have been satisfactory as corrosion inhibitors at temperatures of 150° F or higher, such as are found in petrochemical and oil refinery operations. Substitutes are available for less critical applications, such as air conditioners and cooling towers operating at 120° F or less, but they result in a performance and price penalty.

Wood Treatment Compounds

Sodium dichromate is used to make copper-chromium-arsenic compounds to protect wood against termites, fungus, etc. Other preservatives such as creosote and pentachlorophenol can be used to treat wood but in some cases would result in a performance penalty, primarily in paintability.

Chemical Manufacture and Other Uses

Sodium dichromate is used to manufacture other chemicals such as potassium dichromate, chromium organic complexes for treating textiles and paper, chromium dioxide for magnetic tapes, and chromium-containing catalysts for the synthesis of ammonia and methanol and for many hydrogenation and polymerization reactions. In most cases no substitute is

known for these specific chromium uses, and the elimination of chromium would result in a performance penalty in practically all cases.

SUPPLY ALTERNATIVES

Domestic (18, 51-52)

The Bureau of Mines assessed the viability of 34 nonlaterite and 9 nickeliferous laterite deposits of chromite in the United States. Although some of these deposits have been in production in the past, none of them was considered suitable for development with existing technology at current market prices--domestic production of metallurgical- and chemical-grade chromite would require chromite market prices of about twice those prevailing in January 1981. The minimum lead time required to bring the various operations on-stream ranges from 1 to 4 yr, and, based on domestic resource estimates, production would be relatively small and of short duration. Most of the U.S. chromium resources occur in the Stillwater Complex in Montana as stratiform deposits, in northern California as podiform deposits, and in the Oregon Beach Sands as placer deposits.

Foreign (18, 39, 45, 52-54)

Although world chromite reserves are substantial, they are highly concentrated in southern Africa--over 90 pct are held by the Republic of South Africa and Zimbabwe. Only a few countries, nearly all of which are in the eastern hemisphere, produce significant amounts of chromite (table 7), and of those, the U.S.S.R. and the Republic of South Africa are by far the leading producers, together approaching 60 pct of the total. From another perspective, centrally planned economy countries (essentially the U.S.S.R. and Albania) account for about 40 pct of world production. Present sources that appear capable of continuing as large producers of chromite well into the next century include the Republic of South Africa, Zimbabwe, the U.S.S.R., India, and Finland (54). Announcements by several other countries of new chromite discoveries and projects to expand existing capacity have increased the likelihood of modest decentralization of supply over the next decade or two. However, the vast chromite resources of southern Africa should ensure eventual concentration of production in that region.

The widespread adoption of argon-oxygen-decarburization (AOD) process steelmaking opened the high-iron-content chromite of the Republic of South Africa to metallurgical use (and effectively blurred the traditional distinction among metallurgical-, refractory-, and chemical-grade ores). Whereas ferrochromium production had long been restricted to metallurgical-grade ore with its high chromium-to-iron ratio, AOD permits the utilization of high-carbon ferrochromium (made from high-iron chemical-grade chromite) rather than the costlier low-carbon ferrochromium.

Conversion of chromite to ferrochromium is being accomplished increasingly in the ore-producing countries, as is the construction and planning of new ferrochromium capacity, to accommodate both captive needs and export markets. This is occurring at the expense of some of the traditional ferrochromium producers (who are also the principal consumers)--the United States, Western Europe, and Japan. The top chromite producers, the U.S.S.R. and the Republic of South Africa, are also the world's largest producers of ferrochromium, nearing half of the total, followed by Japan and Sweden. Not surprisingly, Zimbabwe also has established itself as a major ferrochromium supplier. It is probable that world ferrochromium production capacity also will predominate in southern Africa in the long term.

Stockpile (52)

Inventories of metallurgical-, chemical-, and refractory-grade chromite ore are all well below National Defense Stockpile goals. However, an inventory of chromium ferroalloys in excess of the goal is held for offset against chromite. It was announced in December 1982 that the General Services Administration (GSA) would begin a program of upgrading stockpiled chromite into high-carbon

ferrochromium, and in June 1983 GSA solicited bids to convert 125,000 st of stockpiled chromite into ferrochromium.

A panel of industry experts assembled by the American Society for Metals at the request of the U.S. Department of Commerce conducted a quality assessment of the 7.5 million lb of chromium metal in the National Defense Stockpile. The panel concluded that the chromium metal held in the stockpile is not suitable for producing vacuum-melted superalloys for aircraft jet engines or other alloys which have stringent purity requirements for chromium metal as an alloying element. The panel also noted that the stockpile contains no high-purity ferrochromium usable for aircraft superalloys (55).

SUMMARY OF DEMAND AND SUPPLY ALTERNATIVES

Current U.S. chromium consumption could be reduced by approximately one-third by using available technology to substitute alternative materials and processes, to recover and recycle waste chromium, and to design for greater chromium efficiency.

Chromium is essential for corrosion and oxidation resistance in stainless steels, but chromium savings can be accomplished in various stainless steel applications by partially replacing the chromium in excess of 12 pct with other alloying elements, by completely replacing stainless steel with a different metallic or nonmetallic material, by employing thinner gauge or longer lasting high-chromium alloys, or by using surface modification techniques such as cladding, plating, and coating.

Stainless steel scrap is the major source of secondary chromium supply. Although there is considerable chromium in the waste products of some other metallurgical industry processes, collection and processing costs hinder economical recovery on a large scale.

The chromium content of alloy steels can be eliminated or reduced by using other alloying elements that also have a strong influence on hardenability. However, no substitutes are available for existing ultra-high-strength or pressure vessel plate steels.

Chromium plays an important role in the hardness and wear resistance of tool steels. Substitution with sintered carbides entails serious cost penalties.

Low- or no-chromium alternatives are available for roll, abrasion-resistant, and engineering alloy cast irons.

The presence of chromium in superalloys markedly improves resistance to oxidation and hot corrosion. However, the high chromium content is essential only at the surface, not for the mechanical properties of the material.

In alloys of aluminum, titanium, and copper, chromium is used primarily to control microstructure and improve properties, but substitutes for chromium are readily available.

Continuous casting results in significantly higher product yields. Its use in conjunction with the AOD process has been credited with improving chromium yield in stainless steels by 10 to 15 pct.

Wider application of duplex refining systems for steel production appears to be a promising process area for achieving substantial conservation of chromium.

Powder metallurgy techniques as rapid solidification and near-net-shape offer possibilities for chromium conservation by producing unique properties via alloy microstructure and by generating less scrap.

The importance of chrome-bearing refractories has diminished because of the continuing decline in open-hearth furnace steelmaking.

Replacement of chromium pigments with proven alternatives would incur a substantial cost penalty or limit the number of available colors.

No practical substitutes exist for the chromium compounds that are used to tan the bulk of leather produced in the United States.

The chromium used for decorative electroplating could be replaced by chromium-free materials such as plastics, or by painting the substrate. Electroless nickel provides an alternative to hard chromium plating.

No satisfactory substitutes exist for chromium compounds used in deep-well drilling muds.

No chromium-free substitutes have been proven satisfactory as corrosion inhibitors at temperatures of 150° F or higher such as are found in petrochemical and oil refining operations. Alternatives are available for less critical applications.

Nonchromium wood preservatives are readily available, but do not offer comparable paintability.

Although some domestic chromite deposits have been in production in the past, none is considered suitable for development with existing technology at current market prices.

The known chromite resources of the Republic of South Africa and Zimbabwe are so vast that eventual concentration of supply there is expected.

With the trend toward conversion of chromite to ferrochromium in the ore-producing countries, it is probable that future world ferrochromium production will also become highly concentrated in the Republic of South Africa and Zimbabwe.

MANGANESE

BACKGROUND

The importance of manganese arises mainly from its desulfurizing, deoxidizing, and alloying functions in ironmaking and steelmaking, which account for about 90 pct of its use. The minor areas of manganese use are dry cell batteries and chemicals (tables 9 and 10). Manganese ore products containing 35 pct or more Mn have not been produced domestically since 1970. Some manganese is produced in the form of low-grade (10 to 14 pct) manganiferous ores, but it satisfies only a very small amount of U.S. primary demand. The principal sources of recent manganese ore imports are Gabon, the Republic of South Africa, Brazil, Australia, and Mexico. Manganese ore was the dominant form in which manganese was imported until 1977. Imports of manganese in upgraded forms, consisting for the most part of high-carbon ferromanganese, have since been markedly greater than those of ore (table 11). The Republic of South Africa and France presently are the leading suppliers of manganese ferroalloys to the United States. (The implications for the domestic ferroalloy industry regarding the shift in imports from ore to processed form have been discussed previously.) At current prices there are no reserves of manganese ore in the United States containing 35 pct or more Mn or from which concentrates of such a grade could be commercially produced. Although technology for making ferromanganese from lower grade ores is available, the use of high-manganese content ores is far more cost effective.

TABLE 9. - Consumption of manganese ore in the United States[1]

(Thousand short tons)

Use	1981	1982	1983
Manganese alloys and metal.....	745	412	274
Pig iron and steel....	148	84	106
Batteries, chemicals, and miscellaneous....	184	113	151
Total.....	1,077	609	531

[1]Containing 35 pct or more manganese (natural).

In 1983, the total consumption of manganese in the United States declined to 668,000 st, the lowest quantity since before 1960, and far below the high of 1,554,000 st in 1973. As with chromium, the recent sharp decline in manganese demand paralleled the drop in output of the steel industry. A representative average price for metallurgical ore containing 48 pct Mn was about $1.38 per long ton unit, c.i.f. U.S. ports in 1983, down from $1.58 in 1982. The average annual growth rate to the year 2000 for manganese demand in the United States is forecast at 1.6 pct (base year 1981).

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TABLE 10. - Consumption by end use of manganese ferroalloys and metal in the United States

(Thousand short tons, gross weight)

End use	Ferromanganese	Silicomanganese	Manganese metal
1981			
Carbon steel	621	95	6
Stainless steel and heat-resisting steel	12	5	3
Full-alloy steel	105	31	1
High-strength low-alloy steel	60	10	1
Electric steel	(1)	(1)	(1)
Tool steel	(1)	(1)	(1)
Cast iron	17	9	(1)
Superalloys	W	W	(1)
Other alloys	2	3	11
Miscellaneous and unspecified	2	2	1
Total[2]	821	156	24
1982			
Carbon steel	329	67	5
Stainless steel and heat-resisting steel	8	3	2
Full-alloy steel	45	18	1
High-strength low-alloy steel	37	7	1
Electric steel	(1)	(1)	(1)
Tool steel	(1)	(1)	(1)
Cast iron	13	8	(1)
Superalloys	W	W	(1)
Other alloys	2	2	8
Miscellaneous and unspecified	4	1	(1)
Total[2]	439	106	17
1983			
Carbon steel	335	50	6
Stainless steel and heat-resisting steel	15	4	2
Full-alloy steel	38	13	1
High-strength low-alloy steel	37	5	1
Electric steel	(1)	(1)	(1)
Tool steel	(1)	(1)	(1)
Cast iron	15	8	(1)
Superalloys	W	W	(1)
Other alloys	1	1	8
Miscellaneous and unspecified	4	(1)	1
Total[2]	446	83	18

W Withheld to avoid disclosing company proprietary data; included with Miscellaneous and unspecified.

[1]Less than 1/2 unit.

[2]Data may not add to totals shown because of independent rounding.

TABLE 11. - Domestic production and imports of manganese ferroalloys and manganese ore

(Thousand short tons)

Year	Manganese ferroalloys[1]				Manganese ore: Imports	
	Domestic production		Imports		Gross weight	Mn content
	Gross weight	Mn content[e]	Gross weight	Mn content		
1963.....	[e]922	695	[e]173	131	2,390	1,124
1973.....	893	688	438	336	1,510	722
1981.....	390	292	808	615	639	301
1982.....	207	163	560	430	238	111
1983.....	[2]86	[2]70	488	364	368	178

[e]Estimated.

[1]Includes ferromanganese, silicomanganese, and manganese metal.

[2]Ferromanganese only; silicomanganese and manganese metal production data withheld to avoid disclosing company proprietary data.

World production of manganese, world manganese reserves, and exports to the United States are contained in table 12.

USES AND DEMAND ALTERNATIVES

Metallurgical (56-63)

Iron and Steel

Manganese is consumed both in ironmaking and steelmaking (fig. 1). The use of iron ore with a low manganese content requires additional manganese in the blast furnace for desulfurization, usually as some combination of manganese-containing iron ore, low-grade manganese ore, high-grade manganese ore fines, recycled slag, and scrap. Some manganese loss occurs in the slag, and, to a lesser extent, in the flue dust. The optimal hot-metal manganese level of 0.6 to 0.8 pct provides several beneficial effects during steelmaking, such as enhanced desulfurization, increased yield, longer refractory life, and reduced flux consumption. Much of the manganese in the hot metal is lost during steel production, primarily to the slag.

Molten steel contains dissolved sulfur and oxygen which generally impart undesirable properties if retained in the solidified steel. In the steelmaking process manganese ferroalloys are added either mostly in the furnace (open hearth) or after the metal has been tapped into the ladle (basic oxygen converter and electric furnace) in order to perform the essential roles of taking the sulfur and oxygen into the slag or combining with them in a more benign form in the final product. However, aluminum and silicon are better deoxidizers, so manganese usually is not used alone for deoxidation. Aside from the function of tying up impurities, manganese improves the mechanical properties of steel by

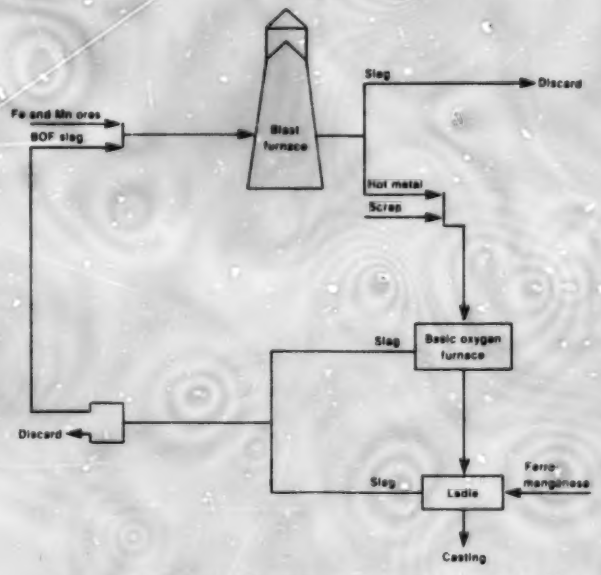

FIGURE 1. - Flowsheet showing manganese inputs for production of steel by blast furnace-basic oxygen process.

TABLE 12. - World manganese mine production, reserves, and U.S. imports

(Thousand short tons except as otherwise noted)

Country	Mine output				Reserves	U.S. imports					
	Mn, pct	1981	1982[P]	1983[e]	(Mn content)	Mn ferroalloys[1,2]			Manganese ore[3,4]		
						1981[5]	1982	1983	1981	1982	1983
Australia	37-53	1,555	1,248	1,491	51,600	6	18	16	66	37	29
Bolivia	28-54	1	(6)	(6)	NA	0	0	0	0	0	0
Brazil	38-50	2,251	2,580	2,300	20,900	12	44	59	76	6	79
Bulgaria	30-	50	50	50	NA	0	0	0	0	0	0
Canada		0	0	0	0	62	20	3	0	4	0
Chile	32-35	28	18	18	NA	0	0	0	0	0	0
China	20+	1,760	1,760	1,760	15,000	5	0	0	0	0	0
France		0	0	0	0	189	104	117	0	0	0
Gabon	50-53	1,640	1,667	2,047	110,000	0	0	0	180	46	171
Germany, Federal Republic of		0	0	0	0	(6)	1	6	0	0	0
Ghana	30-50	246	176	210	4,000	0	0	0	0	0	0
Greece	48-50	6	6	6	NA	0	0	0	0	0	0
Hungary	30-33	78	91	94	NA	0	0	0	0	0	0
India	10-54	1,682	1,596	1,455	21,500	0	10	0	0	0	0
Indonesia	47-56	3	20	19	NA	0	0	0	0	0	0
Italy	30	10	10	10	NA	0	0	0	0	0	0
Japan	24-27	96	86	85	NA	5	6	3	0	0	0
Korea, Republic of		0	0	0	0	(6)	0	0	0	0	0
Mexico	27+	637	561	386	3,500	46	40	42	65	3	64
Morocco	50-53	121	106	81	600	0	0	0	25	9	(6)
Norway		0	0	0	0	5	4	33	0	0	0
Pakistan	35-	(6)	(6)	(6)	NA	0	0	0	0	0	0
Philippines	30+	3	2	2	NA	0	0	0	0	0	0
Portugal		0	0	0	0	33	20	28	0	0	0
South Africa, Republic of	30-48+	5,555	5,750	3,181	407,000	274	255	140	227	132	25
Spain		0	0	0	0	10	0	6	0	0	0
Sudan	48	(6)	(6)	(6)	NA	0	0	0	0	0	0
Thailand	46-50	12	9	7	NA	0	0	0	0	0	0
Turkey	27-46	16	8	4	NA	0	0	0	0	0	0
U.S.S.R.	30-31	10,090	10,830	11,500	365,000	0	0	0	0	0	0
United Kingdom		0	0	0	0	14	17	0	0	0	0
Yugoslavia	+	34	33	33	NA	14	16	26	0	0	0
Zaire	30-5?	20	0	0	NA	0	0	0	0	0	0
Total[7]	NAp	25,894	26,607	24,739	[8]1,000,000	671	555	481	639	238	368

[e]Estimated.
[P]Preliminary.
NA Not available.
NAp Not applicable.
[1]Ferromanganese and silicomanganese.
[2]Average manganese content: 1981--ferromanganese, 77.8 pct; 1982--ferromanganese, 77.9 pct, silicomanganese, 66.2 pct; 1983--ferromanganese, 78.0 pct, silicomanganese, 65.9 pct.
[3]35 pct or more manganese.
[4]Average manganese content: 1981--47.1 pct; 1982--46.7 pct; 1983--48.4 pct.
[5]Ferromanganese only.
[6]Less than 1/2 unit.
[7]Data may not add to totals shown because of independent rounding.
[8]Rounded.

imparting alloying effects of increased strength, toughness, hardness, and hardenability.

The bulk of manganese ferroalloys is consumed in the production of plain carbon steel, and most of the remainder is used in the various alloy steels. With the exception of carbon, manganese is the least expensive means of adding strength to steel, and manganese even replaces carbon in high-strength low-alloy steels since high carbon content can adversely affect other properties. The manganese content of carbon and alloy steels ranges from a few tenths to less than 2 pct; stainless steels usually do not exceed 2 pct Mn, but some require much higher levels; and high-manganese steels, such as Hadfield steel, may contain as much as 14 pct Mn. The surface of Hadfield steel hardens under repeated impact, but its interior retains toughness and is therefore used in railroad applications and mining and earthmoving equipment.

The type of ferroalloy used to add manganese to steel is determined by cost and the technical constraints dictated by the desired products. High-carbon ferromanganese is normally used since it is considered the most economic form. Medium-carbon and low-carbon grades of ferromanganese are necessary where the carbon content of the steel is critical, but if the introduction of carbon could be detrimental, and silicon content is acceptable to the product requirements, silicomanganese is used. Silicomanganese is also less expensive than medium- or low-carbon ferromanganese, and the silicon also acts as a deoxidant, leaving a greater amount of manganese in the steel.

There is no practical substitute for manganese in steelmaking. Potential substitutes for manganese as a steel desulfurizer include zirconium, titanium, and rare earth metals, and possibly calcium and magnesium, but these metals cannot be supplied in sufficient quantities at low prices. Likewise, equivalent properties can be obtained with other alloying metals such as chromium, molybdenum, and nickel, but only at much higher cost.

Past and present developments in steelmaking technology have brought about manganese conservation. The phasing out of open-hearth steelmaking has resulted in a corresponding decline in unit manganese consumption. In the open-hearth process the bulk of manganese ferroalloy is added to the furnace during steelmaking, resulting in considerable manganese losses. With the basic oxygen converter the manganese ferroalloy can be added to the ladle at the same time as other elements, improving the yield. The electric furnace can lower the unit consumption of manganese for a particular type of steel even more by further reducing the loss of manganese to slag through oxidation compared with the other processes.

The unit consumption of manganese as ferroalloys per ton of raw steel produced in the United States in 1982 and 1983 was significantly below the levels of previous years--the 1983 usage rate was about 75 pct of that in 1981. Just a few years ago, such a dramatic reduction over such a relatively short period of time was considered impossible. Although product mix is a relevant factor, the change has happened principally because of the rapid adoption of new steelmaking practices whose benefits include a decrease in manganese processing losses. Most steelmakers have ceased the original refining practice of blowing all the oxygen on the top of the bath. The initial departure from the basic oxygen process (BOP) was the Q-BOP or OBM process in which all the oxygen is blown through bottom tuyeres to provide more efficient mixing and thus achieve higher yields, greater cleanliness, and low carbon levels. A modified form, K-BOP, blows only 40 pct of the total oxygen through the bottom, while the rest is top blown. Since the bottom-blown furnace has high capital requirements, several simpler processes requiring less capital have been developed by various steel companies. They combine top blowing of oxygen and bottom stirring with inert gas. In some cases, bottom stirring is coupled with a small amount of bottom-blown oxygen. In addition to higher manganese residuals, these new technological developments offer higher yields, less flux consumption, better aluminum recovery,

low carbon levels, increased scrap utilization, and better removal of impurities, at lower cost.

It was previously thought that the only opportunities available to lower the specific demand for manganese in steel would be evolutionary changes, such as--

Electric furnace steelmaking, since a higher percentage of electric furnace production capacity would reduce manganese losses from oxidation compared with open-hearth and basic oxygen converter processes.

External desulfurization, which utilizes calcium carbide or magnesium to lower the sulfur content of iron that is to be subsequently processed into steel.

Argon-oxygen decarburization (AOD), which allows better retention of easily oxidized materials such as manganese; extension of AOD to a wider range of alloy and carbon steels would increase the efficiency of manganese utilization.

Direct reduced iron (DRI), since usage in steelmaking furnaces can lower manganese needs because of its low sulfur content.

Continuous casting of raw steel, which increases the yield of steel products and lowers the amount of scrap that must be recycled, thus minimizing remelting (and attendant manganese loss) and increasing the overall efficiency of manganese utilization in the system.

Packaging of manganese alloys, which avoids losses from abrasion and breakage of alloys during handling in the usual bulk form.

Tighter specifications, since manganese content may be broader and higher than necessary to meet property requirements for some grades of steel.

Whereas the recent decline of nearly 25 pct in unit manganese consumption, attributable largely to new steelmaking technology, occurred in only 2 yr, full attainment of the manganese conservation potential of the alternatives listed above, although of similar magnitude (20 to 30 pct), is considered long term. Their conservation potential is probably in the range of 10 to 15 pct in the short term (several years).

Most of the manganese that is lost from the steelmaking system goes to the slag. A portion of the slag is returned to the blast furnace, where some manganese is recovered in the pig iron. The proportion of slag that can be recycled is limited by its phosphorus content because the phosphorus entering the blast furnace ends up in the pig iron and would build up excessively if sufficient slag were not discarded. Steelmaking slags are not a promising potential source for reclamation of manganese. The slags are low in manganese content (4.5 to 9 pct) and are not amenable to direct treatment by hydrometallurgical methods, instead requiring energy-intensive pyrometallurgical or combined pyrometallurgical-hydrometallurgical processing. Also, existing slag dumps are usually intermixed with other refuse.

Most manganese contained in steel scrap is oxidized and lost to slag when scrap is recycled in steelmaking furnaces.

Nonferrous Alloys

Manganese is used as a component of some nonferrous alloys to impart hardness, stiffness, and corrosion resistance. Aluminum alloys containing 1 pct or more manganese are used for beverage cans and food handling equipment. Manganese bronzes (copper-base alloys strengthened by small additions of manganese) are found in marine propellers and fittings, gears, and bearings. High-manganese-content specialty alloys include copper-manganese-nickel electrical-resistance alloys, which contain 10 pct or greater manganese, and alloys with high coefficients of thermal expansion for bimetallic elements of thermostats.

Batteries (62)

Manganese dioxide has long been a component of the common dry-cell battery. Depending on costs and desired battery characteristics, the manganese dioxide that is used may be from certain natural ores, a synthetic form produced by electrolytic or chemical means, or a blend of

both materials. Manganese dioxide had been thought to act as a depolarizer by removing any hydrogen that formed, but according to current theory, it participates directly in the electrochemical reaction of the cell. Substitution with alternative batteries is possible, but for economic reasons only to a limited extent.

Chemicals and Miscellaneous (37, 57, 60, 62)

Manganese ore is used as an oxidant in the production of hydroquinone, which has applications in photographic developers and in the production of certain types of rubber and plastic. Ore is also employed as a decolorizing agent to neutralize the iron content common in most glass sands.

Potassium permanganate is a powerful oxidant frequently utilized in water treatment and purification, as well as a variety of other chemical applications. Manganese dioxide is used in the sealant of incandescent light bulb bases, and as part of the frits for bonding glass and porcelain to metal. Manganous oxide is utilized as an additive to livestock and poultry feeds, and as a component of welding rods and fluxes. Manganese sulfate is used as a fertilizer supplement; manganese chloride as a textile dye and a magnesium alloy flux; and manganese persulfate as an oxidizing agent in the synthesis of organic compounds. Substitution is possible for some of the oxidant, chemical, and miscellaneous uses of manganese, but seldom where requirements call for the metal itself.

SUPPLY ALTERNATIVES

Domestic (56, 62, 64)

The Bureau of Mines investigated the availability of manganese from eight known domestic occurrences (table 13). These deposits were found to have demonstrated resources totaling 420 million mt, but with an average grade of only 10 pct contained manganese. Principally because of high beneficiation and transportation costs, prices substantially in excess of those currently prevailing in the market would be required for development, in the absence of a major cost-reducing technological breakthrough. Although annual production of domestic ore could theoretically reach a maximum of 900,000 mt of recoverable manganese, the lag time in bringing these individual sites on-stream would range from 3 to 6 yr.

Since manganese can be moved and concentrated readily in a number of geologic environments, many undiscovered concentrations may exist. However, its lack of a distinctive geophysical expression and its abundance in subeconomic concentrations hinder standard geophysical and geochemical exploration techniques. On the basis of geologic inference, it has been suggested that the possibility of sizable, high-grade, U.S. deposits is greatest in the Atlantic and Gulf Coastal Plains and in the North Central States, but the level of understanding of ore formation is inadequate to predict a sufficiently small region of high potential.

TABLE 13. - Domestic manganese resources

Mine	State	Ore grade, pct	Demonstrated resources, 10^3 mt
Hanshell Mine.....	AZ	15.0	5,895.5
Maggie Mine.....	AZ	8.75	8,441
Sunnyside Mine.....	CO	10.0	24,909
Maple Mountain-Hovey Mountain..	ME	8.87	260,000
North Aroostook District (Dudley and Gelot Hill).....	ME	9.54	63,100
Cuyuna North Range (SW portion)	MN	7.84	48,960
Butte District (Emma Mine).....	MT	18.0	1,232
Three Kids Mine.....	NV	13.2	7,230

Foreign (56-57, 62, 65-66)

There is no shortage of manganese worldwide--adequate reserves exist to meet foreseeable needs, but they occur primarily in the Republic of South Africa and the U.S.S.R. These nations are currently the two largest producers of manganese ore. Although much of its production is considered submarginal by market economy standards, the U.S.S.R. prefers to meet its manganese requirements internally and provides most of the manganese consumed by the other centrally planned economy countries as well. However, these countries have been increasing their imports of manganese from non-Soviet sources. In the future, market economy countries will likely continue to depend on a few suppliers for most of their manganese ore. The prominence of the Republic of South Africa is expected to increase because of its resource position and relatively cheap energy. Gabon, whose metallurgical-grade ore is among the richest in the world, will be able to increase output by nearly 50 pct when the Trans-Gabon Railroad is completed. Australia should also continue as a leading ore producer and export. Brazil's principal mine, Serra do Navio, will be depleted of reserves in the next decade, and while deposits in the Carajas region promise to fill the void, ore exports from that source are expected to be limited in favor of conversion to manganese ferroalloys for export and captive use. India's role as a major ore supplier could diminish somewhat because of internal needs, depending on developments in the Indian steel and ferroalloy industries. While presently a moderate-scale world producer of relatively low-grade carbonate ore, Mexico has sufficient deposits to support a substantial increase in production. Mexico thus appears to offer an opportunity for a secure, accessible, alternative source of manganese for the United States, although the ore requires roasting and blending with higher grade material.

As with chromium, primary raw material supplies, i.e., manganese ore, may no longer be the main concern for the United States, because imports of manganese are increasingly in the form of ferroalloy. There is a clear and accelerating trend to convert ore to manganese ferroalloys by the ore-producing countries at the expense of production capacity in the United States. Of the major ore producers, only Gabon has no ferroalloy capacity as yet. Without adequate or alternative U.S. manganese ferroalloy capacity, the issue of a secure source of manganese has a different connotation. The major world producers of manganese ferroalloys are the U.S.S.R., Japan, China, the Republic of South Africa, Norway, and France.

Ocean Minerals (56)

Typical deep-sea nodules contain 25 to 35 pct Mn on a dry basis, and the resource potential of marine manganese crusts is currently being assessed. Previous discussion has touched on the present impediments to ocean mining.

Stockpile (62)

Provided that the National Defense Stockpile materials are satisfactory for their intended purposes, quantities of chemical- and battery-grade manganese in inventory were in excess of stockpile goals, except for synthetic manganese dioxide. The inventory of metallurgical ore stood at 89 pct of the goal as of November 30, 1983, but the shortfall could be more than met by offset credits from inventories of ferroalloys and metal in excess of goals.

In December 1982, it was announced that a portion of stockpiled manganese ore would be upgraded into high-carbon ferromanganese as part of a program to improve stockpile readiness and to maintain some domestic ferroalloy capacity. The plan called for the production of about 577,000 st of ferromanganese over a 10-yr period. In 1983 and 1984, GSA contracted for upgrading a total of approximately 128,000 st of ore.

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SUMMARY OF DEMAND AND SUPPLY ALTERNATIVES

The bulk of manganese consumed in the United States (about 90 pct) is used for its desulfurizing, deoxidizing, and alloying functions in ironmaking and steelmaking.

The universal use of manganese in steelmaking results from its abundant supply and its low cost relative to that of other materials and of modified steelmaking practices that might accomplish the same ends. From a practical standpoint there is no substitute for manganese.

The phasing out of open-hearth steelmaking has resulted in a corresponding decline in unit manganese consumption. Both the basic oxygen converter and the electric furnace result in improved yields of manganese.

The adoption of new steelmaking practices that combine top blowing of oxygen and bottom stirring with inert gas has been a major factor in reducing the unit consumption of manganese as ferroalloys per ton of raw steel produced by nearly 25 pct in only 2 yr.

Other technological opportunities capable of lowering the specific demand for manganese per ton of steel are evolutionary changes, not breakthroughs. Full attainment of the manganese conservation potential of these alternatives could reduce the unit manganese consumption by 20 to 30 pct. In the short run (several years) their conservation potential is probably in the range of 10 to 15 pct.

Most of the manganese that is lost from the steelmaking system goes into the slag, but the proportion of slag that can be recycled is limited by its phosphorus content. Steelmaking slags are also not a promising potential source for economical reclamation of manganese because of their low manganese content and lack of amenability to direct hydrometallurgical treatment methods.

The quantity of manganese used in the United States for purposes other than ironmaking and steelmaking (nonferrous alloys, batteries, chemicals) amounts to only about 10 pct of demand.

Domestic manganese deposits contain low-grade ore and would require market prices substantially in excess of those currently prevailing to warrant development. Bringing the individual sites onstream would require from 3 to 6 yr.

Mexico appears to offer an opportunity for a secure, accessible, alternative source of manganese ore for the United States.

There is an accelerating trend to convert manganese ore to manganese ferroalloys by the ore-producing countries, at the expense of production capacity in the United States and other consuming nations. U.S. imports of manganese ferroalloys now substantially exceed those of manganese ore.

PLATINUM-GROUP METALS

BACKGROUND

The platinum-group metals consist of platinum, palladium, iridium, osmium, rhodium, and ruthenium. They exhibit several remarkable properties including resistance to corrosion and oxidation even at high temperatures; extensive and sometimes unique catalytic activity; high melting points; and great strength. As a result, they are used as automotive, chemical process, and petroleum refining catalysts, and in electrical devices, dental supplies, jewelry, and glass manufacturing. Of the six metals comprising the group, palladium and platinum together account for approximately 90 pct of consumption (table 14). In spite of the high initial cost, platinum-group metals continue to be used because they are generally superior to other less expensive or more widely available materials, and in nondissipative uses, they exhibit excellent recyclability (table 15).

A very small quantity of platinum-group metals is derived from domestic copper mining as a byproduct. About 10 pct of the annual supply consists of recycled metal. The remainder is imported, mostly as refined metal from the Republic of South Africa, the U.S.S.R., and the United Kingdom. The latter refines some

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TABLE 14. - Platinum-group metals sold[1] to consuming industries in the United States

(Thousand troy ounces)

Use	Pt	Pd	Ir	Os	Rh	Ru	Total[3]	
							Quantity	pct
1981								
Catalysts:								
Automotive	447	129	(2)	0	30	1	607	32
Petroleum	88	21	2	0	0	(2)	111	6
Chemical	78	90	1	(2)	9	52	231	12
Electrical	112	345	4	0	12	27	500	26
Glass	29	3	0	0	4	0	36	2
Jewelry	28	15	1	0	4	1	47	2
Dental-medical	19	255	(2)	(2)	(2)	(2)	275	14
Miscellaneous	72	30	1	0	4	6	114	6
Total[3]	873	889	8	1	62	88	1,921	100
1982								
Catalysts:								
Automotive	478	118	(2)	0	26	0	623	33
Petroleum	22	21	1	0	(2)	0	43	2
Chemical	64	129	1	(2)	7	64	264	14
Electrical	90	312	5	0	9	21	438	23
Glass	21	(2)	(2)	0	2	0	23	1
Jewelry	16	8	1	0	3	(2)	29	2
Dental-medical	23	311	(2)	1	(2)	(2)	335	18
Miscellaneous	68	27	2	0	2	20	118	6
Total[3]	780	926	11	1	50	105	1,873	100
1983								
Catalysts:								
Automotive	508	172	(2)	0	20	0	700	37
Petroleum	38	50	1	0	0	(2)	89	5
Chemical	65	40	1	(2)	4	55	165	9
Electrical	75	250	1	0	8	71	406	21
Glass	15	(2)	(2)	0	2	0	17	1
Jewelry	10	7	1	0	2	1	21	1
Dental-medical	17	344	(2)	1	(2)	(2)	362	19
Miscellaneous	68	60	1	0	8	17	154	8
Total[3]	797	922	5	1	44	145	1,914	100

[1]Primary and non-toll-refined secondary metals.
[2]Less than 1/2 unit.
[3]Data may not add to totals shown because of independent rounding.

TABLE 15. - Secondary platinum-group metals toll-refined in the United States

(Thousand troy ounces)

Metal	1981	1982	1983	Metal	1981	1982	1983
Pt	521	394	434	Rh	35	27	42
Pd	607	431	457	Ru	18	6	56
Ir	8	10	6	Total[1]	1,191	868	995
Os	2	1	1				

[1]Data may not add to totals shown because of independent rounding.

South African and Canadian material, but world mine production of platinum-group metals is virtually the exclusive domain of the U.S.S.R. and the Republic of South Africa. Recent U.S. net import reliance has been 80 pct or more of apparent consumption.

The consumption of all platinum-group metals totaled 1.914 million tr oz in 1983; the highest level of platinum-group metal consumption was 2.756 million tr oz in 1979. Producer and dealer prices in 1983 were $475/tr oz and $424/tr oz respectively for platinum, and $130/tr oz and $136/tr oz respectively for palladium.

The U.S. demand for platinum-group metals collectively is expected to grow at an average annual rate of 2.9 pct from 1981 to the year 2000. Table 16 contains world production of platinum-group metals, world reserves, and imports by the United States.

USES AND DEMAND ALTERNATIVES

Catalysts

Automotive Emission Control (67-71)

The most significant event affecting the consumption of platinum-group metals in the United States has been their adoption as catalysts for the control of auto exhaust emissions. From 1965 through 1974 the automotive industry was able to comply with exhaust emission standards by engine modifications, but to the detriment of fuel economy and performance. Additional reductions in emissions mandated by more restrictive standards led to the incorporation of catalytic converters in the exhaust system, which allowed the engine to operate with more effective ignition timing, thereby improving economy and performance. Thus, the automotive industry became the single largest consumer of platinum in the United States (while the petroleum industry also had to increase its use of platinum catalysts for the production of lead-free gasoline required by automobiles equipped with converters). Although many potential catalyst materials have been examined since the late 1960's, to date only platinum-group metals, currently combinations of platinum, palladium, and rhodium (average loading ratio 10.3:3.9:1), have shown the necessary efficiency and durability. The possibility that a suitable base-metal catalyst may be developed cannot be discounted, but this would constitute a breakthrough and therefore cannot be predicted to occur at any particular point in time.

Although the metal is virtually intact at the end of a converter's useful life, reclamation of platinum-group metals from catalytic converters presents a complex problem. The combination of low concentrations of precious metals (averaging 0.079 tr oz per unit) and difficulties in converter collection presents technical and logistical challenges. The total amount of precious metals involved is significant--about 6.5 million tr oz of platinum-group metals have been sold to the U.S. automotive industry from 1974 through 1983. Approximately 80 pct of the amount is still contained on operating vehicles, but only 15 to 20 pct of the remainder has been recycled. Complete recycling of all platinum-group metals does not occur because a portion is lost during normal life; not all is recoverable by refiners, especially if the catalyst is contaminated; and many converters are lost to scrap shredders or are being held by speculators. At present, costs are high, the market is speculative, and supply is erratic, but as industry awareness and the efficiency of the collection chain (dismantlers, collectors, decanners, and refiners) improve, recycling should increase. By 1988, an estimated 8.5 million cars per year will be scrapped. One estimate of the extent of platinum-group metal recovery that is possible projects a 70-pct rate (70). Short-term solutions to a lack of platinum-group metal availability, such as a relaxation of emission standards whereby non-precious-metal catalysts could achieve a reduced emission standard or a moratorium on the use of converters, obviously compromise the quality of the environment.

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TABLE 16. - World platinum-group metal production, reserves, and U.S. imports

(Thousand troy ounces)

Country	Production			Reserves	U.S. imports		
	1981	1982[p]	1983[e]		1981	1982	1983
Australia	15	14	14	NA	26	5	20
Belgium-Luxembourg	0	0	0	0	140	107	208
Canada	383	228	167	8,000	78	95	231
China	0	0	0	NA	0	0	7
Colombia	15	20	20	([1])	4	1	7
Costa Rica	0	0	0	0	10	3	4
Ethiopia	([2])	([2])	([2])	NA	0	0	0
Finland	4	9	9	NA	3	6	3
Germany, Federal Republic of	0	0	0	0	19	31	83
Hong Kong	0	0	0	0	53	0	1
Italy	0	0	0	0	3	28	54
Japan	[3]36	[3]43	[3]59	0	1	4	10
Korea, Republic of	0	0	0	0	0	0	1
Mexico	0	0	0	0	79	162	78
Netherlands	0	0	0	0	42	27	35
Norway	0	0	0	0	33	27	17
Panama	0	0	0	0	6	0	0
Peru	0	0	0	0	11	1	0
Singapore	0	0	0	0	0	0	5
South Africa, Republic of	3,110	2,600	2,600	790,000	1,621	1,195	1,219
Spain	0	0	0	0	9	2	6
Sweden	0	0	0	0	6	5	23
Switzerland	0	0	0	0	37	35	61
Taiwan	0	0	0	0	0	0	58
U.S.S.R.	3,350	3,500	3,600	190,000	359	405	430
United Kingdom	0	0	0	0	303	339	639
United States	7	8	6	1,000	0	0	0
Venezuela	0	0	0	0	0	0	15
Yugoslavia	4	3	3	NA	0	0	0
Zimbabwe	8	4	4	([1])	0	0	1
Other	0	0	0	NA	7	18	2
Total[4]	6,931	6,431	6,482	[5]1,000,000	2,850	2,494	3,218

NA Not available. [1]Less than 1 million tr oz.
[2]Less than 1/2 unit. [3]Recovered from imported ore.
[4]Data may not add to totals shown because of independent rounding.
[5]Rounded.

Ceramics present an opportunity for heat engines to operate at temperatures beyond those attainable by current metallic engines. This capability translates into enhanced systems performance in the form of greater fuel economy and substantially reduced emissions. Should ceramics become the material of the future generation of heat engines, there would be a major reduction in the amount of platinum-group metals required to control automotive emissions (28).

Petroleum Refining (67)

The use of platinum-group metals in petroleum refining occurs mostly in hydrocarbon reforming with conventional (platinum) or bimetallic (platinum and rhenium or iridium) catalysts. Other

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refining processes (hydrocracking, isomerization, hydrotreating) are relatively minor uses for platinum and palladium, and the processes rely only partially on these metals for catalysts.

The substitution of other materials, such as molybdenum, for platinum in reforming catalysts would reduce the efficiency of the process. Fortunately, there is a large inventory of platinum-group metals in place. The catalysts are recycled on a toll-refined basis, returned as sponge, and remanufactured into new catalysts. The loss rate is very low (97 pct of the metal in spent refining catalyst is reclaimed), which would enable the petroleum refining industry to continue to operate without the constant need for new metal.

Chemical Processing (67, 72-74)

The oxidation of ammonia to nitric acid is the major chemical process employing platinum-group metal catalysts. Nitric acid is an intermediate in the synthesis of ammonium nitrate (fertilizer, explosives) and is used as a reactant or process chemical in the production of adipic acid (nylon fibers, plastics) and in the synthesis of intermediates which are further processed into compounds such as aniline (rubber, dyes, pharmaceuticals, pesticides) and diisocyanates (polyurethane foams, plastics, elastomers). Nitric acid is also used directly for stainless steel pickling. The catalyst consists of a platinum wire woven into a fine mesh gauze with about 10 pct Rh added to increase strength and efficiency and reduce catalyst losses. Typically a "pack" of 20 gauzes is utilized. Some on-site regeneration of the catalysts can be performed, and metal losses can be recovered (55 to 70 pct) with catchment gauzes and mechanical filters, but after losing a certain percentage of its initial weight, the catalyst is replaced and recycled. An alternative, cobalt oxide with additions of other metal oxides, is available at lower cost, but certain aspects of its performance are inferior. It appears unlikely that platinum gauze will be superseded by this base metal catalyst.

Noble metal catalysts are broadly used elsewhere in the chemical and pharmaceutical industries, but their use in large-scale processes such as organic oxidation (acetaldehyde, acetone, acetic anhydride, acetic acid, vinyl acetate, oxo alcohols), hydrocarbon alkylation and isomerization, and hydrogenation is relatively recent. Often platinum-group metals are not the primary catalysts but rather are used in selective applications. As with petroleum refining catalysts, the recyclability of platinum-group metals utilized as chemical process catalysts is high--about 85 pct.

Electrical and Electronic (67)

These applications depend on the chemical inertness and thermal stability of platinum-group metals and are probably more numerous, involve more product forms, and utilize a wider range of alloy compositions than any other industry. As expected, home scrap and prompt industrial scrap are recycled to a far greater extent than obsolete scrap, although the Department of Defense operates a program to recover platinum-group and other precious metals from surplus, outdated, and damaged Government items.

Contacts

Low-voltage, low-energy contacts, such as found in telephone switching equipment and relays require materials that provide low and stable contact resistance in various environments for as long as 40 yr by exhibiting minimal corrosion and wear. Platinum-group metals, especially palladium, have been used extensively since the lower cost of palladium offsets the generally superior performance of gold. However, replacement of electromechanical devices with electronic switching systems is displacing platinum-group metals from this sector.

Certain contacts (relays, voltage regulators, thermostats, switches, slip-ring assemblies) operate at higher voltages and contact forces and may require better wear and arc erosion resistance. Medium- to heavy-duty relays and switches use platinum alloyed with 5 to 14 pct Ru.

Palladium-silver alloys also are used in this way. For slip-ring assemblies complex platinum-group metal alloys are used as well as electrodeposited rhodium.

Thin- and Thick-Film Circuits

In thin-film circuits and some silicon integrated circuitry, thin layers of platinum or palladium are applied by sputtering or evaporation to provide reliable conductor adhesion. In thick-film and hybrid-integrated circuits, compositions of gold and platinum or palladium, or of palladium and silver, applied as screened-on pastes are used for conductors. Ruthenium applied as a ruthenate paste and converted to ruthenium oxide is used as a resistor material on these circuits. Platinum-group metal use in thick-film and hybrid integrated circuits may be challenged by copper pastes.

Thermocouples and Furnace Components

Various combinations of platinum, rhodium, and iridium are utilized in typical high-temperature thermocouple systems. Ultrapure platinum is used as a resistance thermometer; platinum with 10 to 40 pct Rh is used for windings in furnaces operating to 1,800° C in air; unalloyed platinum and rhodium are used for heater windings.

Electrodes and Miscellaneous

Multilayer ceramic capacitors are a rapidly growing end use for palladium in the form of silver-palladium alloy electrodes. However, lower cost nickel and lead alternatives are being evaluated.

Ruthenium oxide is used as a coating on dimensionally stable titanium anodes used in the production of chlorine and caustic soda. Platinum and platinum-palladium alloys are used as insoluble anodes for the cathodic protection of ships and pipelines. Materials for spark plug electrodes include platinum with 4 pct W, platinum-rhodium alloys, and iridium (especially in heavy-duty aircraft engine spark plugs). Fine platinum-iridium wire is used as fuse wire for explosive detonators.

Glass (67, 75)

Platinum and platinum-rhodium alloys are used in a wide variety of glass handling and forming equipment because of their high melting point, hot strength, low oxidation rate, good corrosion resistance, and noncontaminating nature. Pure platinum is used for glass melting tanks, stirrers, and crucibles for melting high-quality optical and special glasses. Platinum with 10 pct Rh is used for the bushings and baskets needed in the production of glass fibers. Platinum with 40 pct Rh is used for crucible liners, structures for conveying molten glass, fiber-optics-forming devices, laser-glass melters, and stirrers for glass homogenization. Iridium is used as an extrusion die material for glasses of high melting points.

Very low metal losses (about 2 to 4 pct) are experienced in these uses. Worn parts are recycled on a toll basis and returned to the industry for fabrication into new parts.

Jewelry (67)

Platinum-group metal alloys, commonly platinum with 10 pct Ir, platinum with 5 pct Ru, platinum with 4 pct Pd, and palladium with 5 pct Ru, are used for jewelry in cast and wrought form for maximum prestige, reliability, and gem retention. Rhodium as a thin electrodeposit is often used over these or silver jewelry to provide added whiteness, wear resistance, and immunity to tarnishing. In addition, a variety of platinum-group metal-containing inks and pastes are used for decoration of china, glass, and ceramics.

Jewelry certainly seems to be an end use that could be easily dispensed with, should the availability of platinum-group metals become limited. Ironically, however, Japanese consumption of platinum for jewelry, which has almost singlehandedly made jewelry the world's largest end use for the metal, has made large quantities of its coproducts available.

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Dental and Medical (67)

Platinum, palladium, and a variety of complex gold-silver-copper alloys that contain these elements find wide use as dental restorative materials and bone prosthetic treatments. Palladium is emerging as the precious metal of choice, replacing gold, platinum, and platinum-iridium alloys because it provides sufficient strength at lower cost. Primary medical uses of platinum-group metals include platinum coordination compounds used in cancer chemotherapy and platinum-iridium alloy body implant probes, electrodes, and needle tubing.

Miscellaneous (67)

Laboratory Apparatus

Because of its resistance to high temperatures and chemical attack, platinum has found many uses in chemical laboratories, including crucibles or boats made from platinum hardened with rhodium for fusions or combustions, electrodes of platinum hardened with iridium for electrolytic methods and electrodepositions, thermocouples, thermistors, instrument components, and research compounds.

Crystal Growth

Platinum, platinum alloys with rhodium or iridium, and iridium find use as crucible materials in the flux and melt growth of single crystals of oxide compounds that melt at high temperatures. These include sapphire for semiconductor substrates, gadolinium-gallium-garnet for bubble memory devices, neodymium-doped yttrium-aluminum-garnet and ruby for optically pumped lasers, synthetic gemstones, and lithium columbate and lithium tantalate modulator and transducer materials.

SUPPLY ALTERNATIVES

Domestic (67, 76-77)

Platinum and palladium are recovered in the United States as byproducts of copper refining, but this production totals only a few thousand troy ounces annually and accounts for less than 1 pct of domestic consumption. The Bureau of Mines investigated the availability of platinum (only) from domestic sources (table 17) and concluded that only one deposit, the Salmon River (Goodnews Bay Mine), was capable of producing platinum at $420/tr oz, the January 1980 producer price. This mine has been the largest producer of primary platinum in the United States, totaling 641,000 tr oz, and it has been estimated that the deposit could yield an additional 500,000 tr oz at a rate of 10,000 tr oz/yr. Production ceased after 1975 but resumed on a limited basis from 1980 to 1982. The Salt Chuck deposit in Alaska has also been an intermittent producer of platinum-group metals, but total mineralized material and demonstrated resources are quite limited.

In 1983, the three companies involved in the exploration of the Stillwater Complex in Montana formed a new three-way partnership to further evaluate the deposit. Factors that have held back the development of the Stillwater Complex include environmental concerns for the surrounding wilderness area, locations of tailings disposal sites, remoteness and climate of the site, and fluctuations in platinum-group metal demand and prices. The companies involved with the deposits in the Duluth Gabbro in Minnesota have ceased exploration activity there. The relative mix of platinum-group metals in both the Stillwater Complex and the Duluth Gabbro greatly favors palladium over platinum (78 versus 18 to 20 pct), which does not correspond well to industrial demand.

The total amount of recoverable platinum potentially available from the U.S. deposits analyzed in the Bureau study

TABLE 17. - Total U.S. platinum resources[1]

(Million troy ounces)

Contained	3
Recoverable	2

[1]Includes Salmon River, AK; Ely Spruce, MN; Minnamax, MN; Stillwater, MT; Anaconda, MT.

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is about 2.3 million tr oz. At assumed production capacities, these deposits are capable of producing only 113,000 tr oz annually--less than 15 pct of U.S. requirements.

Foreign (67, 76-77)

Nearly all of the world's reserves of platinum-group metals are in the Republic of South Africa and the U.S.S.R. The grade of the South African deposits enables platinum-group metals to be mined as the principal product, unlike most other occurrences. Canada, the third-largest producer, presents a nearby, secure source of supply, but platinum-group metal production is limited by its status as a byproduct of copper and nickel. Likewise, Australian output is also relegated to a byproduct role. Although production in Colombia occurs as a coproduct of gold and silver, production facilities there are aging. Platinum-group metal deposits in Brazil are not under development.

At present the entire platinum-group metal output of these alternative (to the Republic of South Africa and the U.S.S.R.) countries represents only about 20 pct of U.S. primary demand. It appears that the Republic of South Africa is assured of continuing as the major supplier of platinum-group metals to the United States.

Stockpile (67, 77)

Only three of the platinum-group metals--platinum, palladium, and iridium--are held in the National Defense Stockpile. The inventories of each, however, are considerably below their goals: platinum, 34 pct; palladium, 42 pct; iridium, 26 pct. Since 1982 GSA has purchased a total of 10,900 tr oz of iridium from the stockpile. Strictly speaking, none of the previous stockpile inventories of platinum-group metals meets both the current chemical requirements for purity and physical requirements for form, since the inventory is in bar, plate, or sheet form, in contrast to more recent specifications of metallic sponge, and the purity levels of a portion of the stockpile preclude consumption in the highest purity applications.

SUMMARY OF DEMAND AND SUPPLY ALTERNATIVES

Although many potential auto emission catalyst materials have been examined, only platinum-group metals have shown the necessary efficiency and durability. The development of a suitable base metal catalyst would constitute an unforeseeable breakthrough.

The combination of low concentrations of precious metals and difficulties in converter collection presents technical and logistical challenges to automotive catalyst reclamation. However, it is estimated that a 70-pct metal recovery rate could be achieved.

A relaxation of auto emission standards, or a moratorium on the use of catalytic converters, could accomplish considerable conservation of platinum-group metals in a short time, but such action would comprise environmental quality.

Platinum petroleum-refining catalysts are highly recyclable. Substitute catalysts such as molybdenum reduce process efficiency.

Nitric acid manufacture is the major chemical process employing platinum-group metal catalysts. Some on-site catalyst regeneration can be performed, and recyclability is very good. A lower cost cobalt oxide alternative is available, but certain performance aspects are inferior.

Electrical and electronic applications of platinum-group metals are probably more numerous, involve more product forms, and utilize a wider range of alloy compositions than any other industry. Electronic switching systems, printed circuits, and metals such as gold, silver, and tin-lead alloys offer alternatives in many applications.

Platinum-group metals are utilized in a variety of glass handling and forming equipment, but very low metal losses are experienced in these uses; worn parts are recycled on a toll-refined basis.

Gold and silver could readily substitute for platinum in jewelry uses.

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Many dental and medical applications now using palladium could revert to the traditional material, gold, albeit at much higher cost.

Regardless of price, at assumed production capacities, the combined platinum deposits in the United States could produce less than 15 pct of annual requirements.

Nearly all of the world's platinum-group metal reserves are in the Republic of South Africa and the U.S.S.R. The Republic of South Africa seems assured of continuing as the major supplier of platinum-group metals to the United States.

CONCLUSIONS

COBALT

Current essential cobalt needs are estimated at about 50 pct of present consumption.

Substitution

Superalloys. - Significant amounts of cobalt could be replaced, but costly and time-consuming alloy optimization and engine certification programs would be required.

Magnetic alloys. - An estimated 20 pct of current cobalt use is deemed essential.

Cemented carbides. - Cobalt-free materials cannot be considered as practical general alternatives.

Wear-resistant alloys. - Where cobalt is required, lower cobalt substitutes will suffice.

Tool and maraging steels. - Cobalt-free grades have been developed.

Catalysts. - Hydrotreating is amenable to substitution.

Paint driers. - Elimination or reduction of cobalt would incur substantial penalties in convenience and product quality.

Other chemicals. - A 60-pct reduction in cobalt use could be accomplished.

Processing

Near-net-shape processes can achieve improved yields of usable product.

Recycling

Most in-house and prompt industrial scrap is recycled, and cobalt is generally recovered; obsolete, low-grade, and mixed alloy scrap is not efficiently recycled.

Domestic Supply

Development of domestic deposits would require a cobalt price of $20/lb to $25/lb and could take 5 yr.

Foreign Supply

The most competitive cobalt resources in North America are the nickel deposits of Canada.

CHROMIUM

Current U.S. chromium consumption could be reduced by approximately one-third using available technology.

Substitution

Stainless steels. - Chromium savings can be accomplished by partial replacement of the chromium in excess of 12 pct with other alloying elements, by completely replacing stainless steel with a different metallic or nonmetallic material, by employing thinner gauge or longer lasting high-chromium alloys, or by using surface modification techniques such as cladding, plating, and coating.

Alloy steels. - Chromium content can be eliminated or reduced by using other alloying elements that also influence hardenability.

Tool steels. - Substitution with sintered carbides entails serious cost penalties.

Alloy cast irons. - Low- or no-chromium alternatives are available for roll, abrasion-resistant, and engineering types.

Superalloys. - A high chromium content is essential only at the surface, not for mechanical properties.

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Other alloys. - Substitutes for chromium are readily available in alloys of aluminum, titanium, and copper.

Pigments and paints. - Replacement of chromium with proven alternatives would incur a substantial cost penalty or limit the number of available colors.

Leather tanning. - No practical substitutes exist.

Metal finishing and treatment.- Decorative electroplating could be replaced by chromium-free materials such as plastics, or by painting the substrate; electroless nickel provides an alternative to hard plating.

Drilling mud additives. - No satisfactory substitutes exist for deep wells.

Water treatment compounds. - No chromium-free corrosion inhibitors have been proven satisfactory at temperatures of 150° F or higher; alternatives are available for less critical applications.

Wood treatment. - Nonchromium wood preservatives are readily available but do not offer comparable paintability.

Processing

Wider application of duplex refining systems for steel production appears to be a promising process area for achieving substantial conservation of chromium.

Powder metallurgy techniques, such as rapid solidification and near-net-shape, offer possibilities for chromium conservation by producing unique properties via alloy microstructure and by generating less scrap.

The continuing decline in open-hearth furnace steelmaking has diminished the importance of chrome-bearing refractories.

Recycling

Stainless steel scrap is the major source of secondary chromium supply. Collection and processing costs hinder large-scale recovery from other metallurgical industry processes.

Domestic Supply

No domestic chromite deposits are considered suitable for development with existing technology at current market prices.

Foreign Supply

The known chromite resources of the Republic of South Africa and Zimbabwe are so vast that eventual concentration of supply there is expected. With the trend toward conversion of chromite to ferrochromium in the ore-producing countries, it is probable that future world ferrochromium production will also become highly concentrated in these two countries.

MANGANESE

Substitution

From a practical standpoint there is no substitute for manganese in steelmaking.

Processing

The recent adoption of new steelmaking practices that combine top blowing of oxygen and bottom stirring with inert gas has been a major factor in reducing the unit consumption of manganese.

Full attainment of other technological opportunities could eventually reduce the unit manganese consumption by 20 to 30 pct (in the short run 10 to 15 pct).

Recycling

The recyclability of steelmaking slag is limited by its phosphorus content. Slags are also not a promising potential source for economical reclamation of manganese because of their low manganese content and lack of amenability to direct hydrometallurgical treatment methods.

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Domestic Supply

Domestic manganese deposits contain low-grade ore and would require market prices substantially in excess of those currently prevailing to warrant development.

Foreign Supply

Mexico appears to offer an opportunity for a secure, accessible, alternative source of manganese ore for the United States.

There is an accelerating trend to convert manganese ore to manganese ferroalloys by the ore-producing countries at the expense of production capacity in the United States and other consuming nations.

PLATINUM-GROUP METALS

Substitution

Automotive emission control catalysts. - The development of a base metal catalyst with suitable efficiency and durability would constitute an unforeseeable breakthrough.

Petroleum refining catalysts. - Substitutes such as molybdenum reduce process efficiency.

Chemical processing catalysts. - A lower cost cobalt oxide alternative is available for nitric acid production, but certain performance aspects are inferior.

Electrical and electronic. - Electronic switching systems, printed circuits, and metals such as gold, silver, and tin-lead alloys offer alternatives in many applications.

Jewelry. - Gold and silver could readily substitute for platinum.

Dental and medical. - Many applications now using palladium could revert to the traditional material, gold, albeit at much higher cost.

Recycling

The combination of low concentrations of precious metals and difficulties in converter collection presents technical and logistical challenges to automotive catalyst reclamation.

Platinum petroleum refining and chemical processing catalysts are highly recyclable.

Very low metal losses are experienced in glass handling and forming equipment; worn parts are recycled on a toll-refined basis.

Regulations

A relaxation of auto emission standards or a moratorium on the use of catalytic converters could accomplish considerable conservation of platinum-group metals in a short time, but such action would compromise environmental quality.

Domestic Supply

At assumed capacities, production from U.S. platinum deposits would be capable of satisfying less than 15 pct of annual domestic requirements.

Foreign Supply

Nearly all of the world's platinum-group metal reserves occur in the Republic of South Africa and the U.S.S.R.

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